(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
13 August 2020 (13.08.2020)

(10) International Publication Number
WO 2020/163762 A1

(51) International Patent Classification:
*G03F 7/32* (2006.01) *G03F 7/029* (2006.01)
*G03F 7/42* (2006.01) *H01L 51/00* (2006.01)

(21) International Application Number:
PCT/US2020/017293

(22) International Filing Date:
07 February 2020 (07.02.2020)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/802,478 07 February 2019 (07.02.2019) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

**Published:**

— *with international search report (Art. 21(3))*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(54) **Title:** FLUOROPOLYMER RESIST STRUCTURES HAVING AN UNDERCUT PROFILE

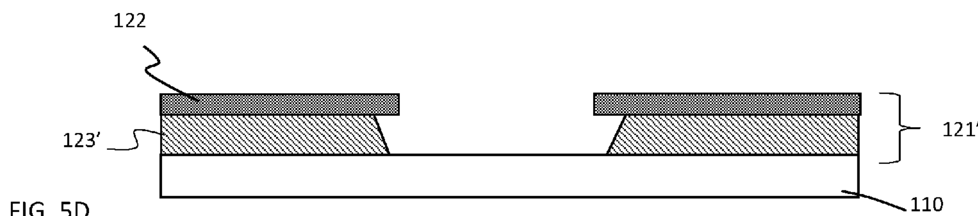


FIG. 5D

(57) **Abstract:** Methods of forming a fluoropolymer resist structure having an undercut profile are disclosed. A patterned precursor structure is formed including a fluoropolymer layer having a pattern of first and second surface regions. The patterned precursor structure is contacted with an undercut developing agent including a hydrofluoroether solvent, a perfluorinated solvent or both. The undercut developing agent removes a portion of the fluoropolymer layer in registration with the first surface region, thereby forming a first patterned fluoropolymer structure having a first undercut profile. The first patterned fluoropolymer structure is contacted with a rinse agent comprising a fluorinated rinse solvent. The fluoropolymer layer has a dissolution rate in the undercut developing agent that is at least 3 times greater than a dissolution rate in the rinse agent. The fluoropolymer resist structures may be used to pattern organic electronic devices such as OLED devices by lift-off processing.

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# FLUOROPOLYMER RESIST STRUCTURES HAVING AN UNDERCUT PROFILE

This application is being filed on February 7, 2020, as a PCT International
5 Patent application and claims the benefit of priority to U.S. Provisional patent application Serial No. 62/804,478, filed February 7, 2019, the entire disclosure of which is incorporated by reference in its entirety.

## BACKGROUND

10 The present disclosure relates to forming fluoropolymer resist structures suitable for patterning devices such as organic, electronic and organic electronic devices. The disclosed methods and materials may be used for lift-off patterning of organic electronic devices, e.g., for forming OLED devices.

Organic electronic devices may offer significant performance and price
15 advantages relative to conventional inorganic-based devices. As such, there has been much commercial interest in the use of organic materials in electronic device fabrication. For example, displays based on organic light-emitting diode (OLED) technology have recently gained popularity and offer numerous advantages over many other display technologies. Although solution-deposited OLED materials have been
20 developed, the highest-performing OLED devices typically use vapor-deposited thin films of active organic materials.

A key challenge for full-color OLED displays is patterning the array of red, green and blue pixels. For vapor-deposited OLEDs, a fine metal mask having openings corresponding to the fineness of the desired pattern is conventionally used.
25 However, a vapor deposited film builds up on the mask which may eventually narrow the mask openings or cause deforming stresses on the mask. Therefore, it is necessary to clean the mask after a certain number of uses, which is disadvantageous from the viewpoint of manufacturing costs. In addition, when a fine metal mask is increased in size to accommodate larger substrates, the positional accuracy of the mask openings
30 becomes much more difficult, both from the standpoint of initial alignment and then maintaining the alignment during deposition due to thermal expansion issues. Positional accuracy may be improved to a degree by enhancing the stiffness of a frame of the mask, but this increase the weight of the mask itself causes other handling difficulties.

Various photolithographic methods have been proposed for patterning organic electronic devices, but the methods have yet to gain commercial acceptance due to materials compatibility and manufacturing robustness issues. Thus, a need exists for robust and cost-effective patterning of organic electronic devices, particularly those 5 having pattern dimensions of less than about 100 μm.

## SUMMARY

The present disclosure relates to materials and methods for forming fluoropolymer resist structures that have improved process yield while maintaining 10 compatibility with sensitive organic electronic materials.

In accordance with the present disclosure method of forming a fluoropolymer resist structure having an undercut profile includes: over a device substrate, forming a patterned precursor structure comprising a fluoropolymer layer, the patterned precursor structure having a pattern of first and second surface regions; contacting the patterned 15 precursor structure with an undercut developing agent comprising a hydrofluoroether solvent, a perfluorinated solvent or both, wherein the undercut developing agent removes a portion of the fluoropolymer layer in registration with the first surface region, thereby forming a first patterned fluoropolymer structure having a first undercut profile; and contacting the first patterned fluoropolymer structure with a rinse agent 20 comprising a fluorinated rinse solvent, wherein the fluoropolymer layer has a dissolution rate in the undercut developing agent that is at least 3 times greater than a dissolution rate in the rinse agent.

In accordance with another aspect of the present disclosure, a method of forming a fluoropolymer resist structure having an undercut profile includes: coating a 25 first fluoropolymer layer over a substrate; coating a photosensitive second fluoropolymer layer over the first fluoropolymer layer; exposing the photosensitive second fluoropolymer layer to patterned radiation to form an exposed structure, wherein the photosensitive second fluoropolymer layer of the exposed structure includes exposed and unexposed portions; and forming a patterned precursor structure 30 by applying a first developing agent to the exposed structure to form a patterned second fluoropolymer layer, the first developing agent comprising a mixture of a first fluorinated solvent and a second fluorinated solvent, wherein, when measured in neat first or second fluorinated solvents at 20 °C, i) the first fluoropolymer layer has a

higher dissolution rate in the first fluorinated solvent than in the second fluorinated solvent, and ii) the unexposed portion of the second fluoropolymer layer has higher dissolution rate in the second fluorinated solvent than in the first fluorinated solvent.

In accordance with another aspect of the present disclosure, an organic
5 electronic device such as an active matrix OLED includes a pixel definition layer, the pixel definition layer including a fluorinated polymer having carboxylic acid groups.

BRIEF DESCRIPTION OF DRAWINGS

10 FIG. 1A is a plan view of a fluoropolymer resist structure having an undercut profile according to an embodiment of the present disclosure.

FIG. 1B is a cross-sectional view of the fluoropolymer resist structure of FIG. 1A along cut line A-A according to an embodiment of the present disclosure.

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FIG. 2 is a series (2A – 2E) of cross-sectional views depicting various stages in the formation of a fluoropolymer resist structure according to an embodiment of the present disclosure.

20 FIG. 3 is a cross-sectional view of a patterned fluorinated photopolymer according to an embodiment of the present disclosure.

FIG. 4A is a plan view of a fluoropolymer resist structure having an undercut profile according to an embodiment of the present disclosure.

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FIG. 4B is a cross-sectional view of the fluoropolymer resist structure of FIG. 4A along cut line B-B according to an embodiment of the present disclosure.

FIG. 5 is a series (5A – 5D) of cross-sectional views depicting various stages in
30 the formation of a fluoropolymer resist structure according to an embodiment of the present disclosure.

FIG. 6 is cross-sectional view of a representative OLED device.

FIG. 7A is a plan view of an active matrix OLED substrate according to an embodiment of the present disclosure.

FIG. 7B is a cross-sectional view of the active matrix OLED substrate of FIG. 7A along cut line C-C according to an embodiment of the present disclosure.

FIG. 8 is a series (8A – 8D) of cross-sectional views depicting various stages in the formation of an active matrix OLED device according to an embodiment of the present disclosure.

FIG. 9 is a plan view of a fluoropolymer resist structure over an active matrix OLED substrate according to an embodiment of the present disclosure.

FIG. 10 is a plan view of a fluoropolymer resist structure over an active matrix OLED substrate according to another embodiment of the present disclosure.

## DETAILED DESCRIPTION

It is to be understood that the attached drawings are for purposes of illustrating the concepts of the disclosure and may not be to scale.

Certain embodiments shown in the present disclosure are directed to preparing a patterned fluoropolymer structure having an undercut profile. Such fluoropolymer structures can be used as a resist for patterning devices. In some embodiments, the fluoropolymer structures and processing agents used to form them are compatible with sensitive electronic devices and materials such as organic electronic devices and materials, i.e., they are chosen to have low interaction with sensitive device layers that are not intended to be dissolved or otherwise damaged. Such fluoropolymer structures are sometimes referred to as “orthogonal” resists.

Conventional resist materials typically use harsh organic solvents or strongly caustic developers that can easily damage one or more layers of an organic electronic device, e.g., an OLED device, an organic electronic sensor or other sensitive devices. Some useful orthogonal resist structures and processing agents include fluorinated polymers or molecular solids and fluorinated solvents. Some orthogonal photoresist structures, systems and methods are disclosed in US Patent Application Nos. 12/864,407, 12/994,353, 14/113,408, 14/260,705, 14/260,666, 14/274,816, 14/291,692,

14/335,406, 14/335,476,14/539,574, 15/117,032, 15/501,092, 15/501,109, 15/501,116, 15/631,616, and 15/501,128, the contents of which are incorporated by reference in their entirety for all purposes.

The fluoropolymer structures of the present disclosures may have an undercut
5 profile, which can be advantageous in so-called “lift-off” lithographic patterning, but such structures are also useful in “etch” or other patterning. Orthogonality can be tested by, for example, immersion of a device comprising the material layer of interest into a target composition prior to operation (e.g., into a coating solvent, a developing agent, a lift-off agent, or the like). The composition is orthogonal if there is no serious
10 reduction in the functioning of the device.

Certain embodiments disclosed in the present disclosure are particularly suited to the patterning of solvent-sensitive, active organic materials. Examples of active organic materials include, but are not limited to, organic electronic materials, such as organic semiconductors, organic conductors, OLED (organic light-emitting diode)
15 materials and organic photovoltaic materials, organic optical materials and biological materials (including bioelectronics materials). Many of these materials are easily damaged when contacted with organic or aqueous solutions used in conventional photolithographic processes. Active organic materials may be coated to form a layer, e.g., over a substrate or over a lift-off resist structure. For some active organic
20 materials, such coating can be done from a solution using conventional methods. Alternatively, some active organic materials may be coated by vapor deposition, for example, by sublimation from a heated organic material source at reduced pressure. Solvent-sensitive, active organic materials may also include composites of organics and inorganics. For example, the composite may include inorganic semiconductor
25 nanoparticles (quantum dots). Such nanoparticles may have organic ligands or be dispersed in an organic matrix. The present disclosure is particularly directed towards patterning of OLED devices, but the concepts and methods disclosed herein can be applied to other electronic, optical, organic electronic or bioelectronic devices.

30 Fluoropolymer resist structure having an undercut profile

Single layer embodiments

FIG. 1 shows a plan view (FIG. 1A) and a cross-sectional view along cut line A-A (FIG. 1B) of a fluoropolymer resist structure **101** having an undercut profile according to some embodiments of the present disclosure. The fluoropolymer resist

structure includes a patterned fluoropolymer layer **103** provided over substrate **110** and has a pattern of openings **105** that are smaller at the top of the fluoropolymer structure than an exposed surface **104** of device substrate **110**. This difference in size creates what is commonly referred to as an “undercut” structure. The device substrate may
5 optionally be a multilayer structure having a rigid or flexible support and one or more additional patterned or non-patterned layers. Support materials include, but are not limited to, plastics, metals, glasses, ceramics, composites and fabrics. In an embodiment, the device substrate is for a MEMS device. In an embodiment, the device substrate includes one or more layers of one or more active organic materials that may
10 optionally be in direct contact with the patterned fluoropolymer layer. One non-limiting example of such a device includes an OLED device, but the device may instead be or include an organic electronic sensor (e.g. a fingerprint sensor); an organic photovoltaic, an organic thin-film transistor (OTFT), a touch sensor, a chemical sensor, a bioelectronic or medical device, or the like.

15 In some embodiments, the fluoropolymer resist structure of FIG. 1 can be prepared according to methods disclosed in US Patent No. 9,991,114, incorporated herein by reference in its entirety, and summarized in FIG. 2. Some useful fluorinated photopolymer materials are described in detail later in the “photosensitive fluoropolymer” section.

20 In FIG. 2A, a fluorinated photopolymer layer **111** is provided over device substrate **110**. The lower surface **111L** of the fluorinated photopolymer layer is provided proximate the device substrate, whereas the upper surface **111U** is distal the device substrate. The distance between the lower surface **111L** and upper surface **111U** defines layer thickness **112**.

25 In an embodiment, the fluorinated photopolymer layer includes a copolymer comprising a first repeating unit having a fluorine-containing group, a second repeating unit having a solubility-altering reactive group, and optionally a third repeating unit having a radiation-absorbing dye. In an embodiment, the photosensitive fluorinated material is a negative working photopolymer provided from a composition including a
30 fluorinated solvent, e.g., a hydrofluoroether. The fluorinated photopolymer composition may be applied to a substrate using any method suitable for depositing a photosensitive liquid material. For example, the composition may be applied by spin coating, slot die coating, curtain coating, bead coating, bar coating, spray coating, dip coating, gravure coating, ink jet, flexography or the like. Alternatively, the fluorinated

photopolymer can be applied to the substrate by transferring a preformed fluorinated photopolymer layer from a carrier sheet, for example, by lamination transfer using heat, pressure or both.

In an embodiment, the fluorinated photopolymer layer further includes a photoacid generator compound or a tertiary amine compound or both, which are optionally covalently attached to the copolymer or to another polymer to reduce diffusion of such compounds to the device substrate. In an embodiment, the solubility-altering reactive group is an acid- or alcohol-forming precursor group. In an embodiment, the radiation-absorbing dye acts as a sensitizing dye. In an embodiment, rather than or in addition to having the radiation-absorbing dye provided as a third repeating unit of the copolymer, the radiation-absorbing dye may be provided as a small molecule material or attached to another polymer.

In FIG. 2B, the fluorinated photopolymer layer is exposed to patterned radiation within the spectral sensitivity range of the photopolymer (e.g., light in a range of 300 nm to 450 nm), thereby forming an exposed fluorinated photopolymer layer **115**. The patterned radiation forms areas of differential solubility due to some chemical or physical change caused by the radiation exposure, in particular, to the reacted solubility-altering reactive groups. The exposed fluorinated photopolymer layer **115** is an embodiment of a patterned precursor structure **116** including a fluoropolymer layer having a pattern of first and second surface regions. Patterned radiation can be produced by many methods, for example, by directing exposing radiation **113** through a photomask **114** and onto the photopolymer layer as shown in FIG. 2B. Photomasks are widely used in photolithography and often include a patterned layer of chrome that blocks light. Thus, as shown in FIG. 2C, the exposed photopolymer layer **115** has one or more exposed areas corresponding to openings in the photomask (second surface regions **119**) where light is not blocked and one or more unexposed areas corresponding to light-blocking areas of the photomask (first surface regions **117**). The photomask may be in direct contact or in proximity. When using a proximity exposure, it is preferred that the light has a high degree of collimation if high resolution features are desired. Alternatively, the patterned light can be produced by a projection exposure device. In addition, the patterned light can be from a laser source that is selectively directed to certain portions of the photopolymer layer.

In FIG. 2D, the exposed fluorinated photopolymer **115** (patterned precursor structure **116**) is contacted with an undercut developing agent including a fluorinated

solvent such as a hydrofluoroether. The undercut developing agent removes unexposed areas of the fluorinated photopolymer, i.e., a portion of the fluoropolymer layer in registration with the first surface region, thereby forming a first patterned fluoropolymer structure **101'** having a first undercut profile. In the present embodiment, the first patterned fluoropolymer structure includes a patterned fluorinated photopolymer **118** covering the device substrate (corresponding to the exposed portions) and a complementary second pattern **105** of openings corresponding to the unexposed portions. Contacting with the undercut developing agent can be accomplished by immersion into the undercut developing agent or by coating it with the developing agent in some way, e.g., by spin coating, curtain coating or spray coating. The contacting can be performed multiple times if necessary. In an embodiment, the undercut developing agent includes at least 50% by volume of one or more fluorinated solvents. In an embodiment, the developing agent includes at least 90% by volume of one or more hydrofluoroether solvents.

As shown in FIG. 2E, the first patterned fluoropolymer structure **101'** may be contacted with a rinse agent including a fluorinated rinse solvent to form the desired fluoropolymer resist structure **101** over substrate **110**. In some embodiments, the undercut profile (e.g. the sidewalls of the patterned fluoropolymer **103**) and openings **105** may be modified by the rinse step relative to the first patterned fluoropolymer structure, but most of the formation of the openings and undercut profile occurs in the undercut developer step. The rinse is discussed in more detail later. If necessary, after the rinse, a brief cleaning step may be used to remove residue in the uncovered substrate areas, e.g., oxygen plasma, argon plasma, UV-ozone or the like.

In some embodiments, in order to reliably form an undercut structure that may be easily lifted-off, the fluorinated photopolymer, radiation exposure and developing conditions are selected to meet the following parameters and formula. In particular, the radiation is selected to provide a total exposure dose EXP (mJ/cm$^2$) at an exposure wavelength $\lambda_{exp}$. The fluorinated photopolymer layer is selected to have a thickness $T_f$ (µm), an absorptivity $\alpha$ (absorbance/µm) at $\lambda_{exp}$ and a speed point SP (mJ/cm$^2$, discussed below) under conditions used for the exposing and contacting with the undercut profile developing agent. Further, the above parameters are selected so that a processing factor, P, is in a range of 0.1 to 0.95 wherein P is defined by Equation (1).

$$P = [\log(EXP/SP)] / (\alpha * T_f) \qquad \text{Equation (1)}$$

As seen in FIG. 2D, a lower portion of the patterned of fluorinated photopolymer **118L** (proximate the underlying device substrate) is more soluble in the undercut developing agent and the lift-off agent than an upper portion of the patterned of fluorinated photopolymer **118U**. Not only can this create an undercut in development, the more soluble portion can be relied upon to provide facile lift-off in subsequent steps. In an embodiment, the lower portion **118L** has a dissolution rate in the undercut developing agent or lift-off agent that is at least 5 times higher than a dissolution rate for the upper portion **118U**. In an embodiment, the lower 10% (in terms of film thickness) of the patterned photopolymer **118** has a dissolution rate that is at least 5 times higher than that of the upper 10% of the patterned photopolymer in the undercut developing agent or the lift-off agent. For example, as shown in FIG. 3, if a patterned photopolymer had a total thickness, $T_f$, of 2.0 μm, the lower 10 % would correspond to the portion of the photopolymer from lower surface proximate the device substrate up to 0.2 μm of the film thickness. The upper 10 % would correspond to the portion of photopolymer between 1.8 μm and 2.0 μm away from the lower surface, i.e., the portion of photopolymer 0.2 μm deep relative to the upper surface. In an embodiment, P is in a range of 0.1 to 0.95, alternatively, 0.3 to 0.95, alternatively 0.5 to 0.95, alternatively 0.5 to 0.92, or alternatively 0.6 to 0.92.

In an embodiment, $T_f$ is at least 1.0 μm and $\alpha$ is at least 0.2 absorbance units per micron. Preferably, $T_f$ is at least 1.5 μm and $\alpha$ is at least 0.3 absorbance units per micron. In an embodiment $T_f$ is at least 1.5 μm and $\alpha$ is at least 0.5 absorbance units per micron.

<u>Bilayer embodiments</u>

FIG. 4 shows a plan view (FIG. 4A) and a cross-sectional view along cut line B-B (FIG. 4B) of a fluoropolymer resist structure **121** having an undercut profile according to some other embodiments of the present disclosure. Undercut fluoropolymer resist structure **121** includes a patterned layer **122** provided over patterned fluoropolymer **123**. The patterned layer **122** includes one or more openings **125** that are smaller than an exposed surface **124** of device substrate **110** formed by patterned fluoropolymer **123**. This difference in size creates an “undercut” structure having similar functionality to the fluoropolymer structure of FIG. 1 but using a bilayer format.

An embodiment of forming fluoropolymer resist structure **121** is shown in FIG. 5. Referring to FIG. 5A, a non-patterned fluoropolymer layer **133** is provided over

device substrate **110**. By "non-patterned" it is meant fluoropolymer layer **133** is provided at least in areas over the substrate requiring further patterning to create the desired fluoropolymer resist structure having an undercut. That is, there may be some macroscopic patterning or deposition of the fluoropolymer layer in the desired areas.
5 Non-patterned fluoropolymer layer **133** may be applied by spin coating, curtain coating, bead coating, bar coating, spray coating, dip coating, gravure coating, ink jet, flexography or the like. Alternatively, the non-patterned fluoropolymer may be applied to the substrate by transferring a preformed fluorinated photopolymer layer from a carrier sheet, for example, by lamination transfer using heat, pressure or both.

10 A photosensitive polymer **132** is provided over non-patterned fluoropolymer layer **133** by any conventional method such as those methods previously mentioned. The photosensitive polymer **132** may be a conventional photoresist or a fluorinated photopolymer (also referred to herein as a photosensitive fluoropolymer). In FIG. 5B, the photosensitive polymer **132** is exposed to patterned radiation **130**, e.g., using a
15 shadow mask, an optical projector, a laser or other methods as previously discussed. This creates regions of unexposed photosensitive polymer **132a** and exposed photosensitive polymer **132b**.

In FIG. 5C, the structure from FIG. 5B is contacted with a first developing agent to form a patterned precursor structure **126** including patterned layer **122** and
20 non-patterned fluoropolymer layer **133**. Patterned precursor structure includes a pattern of first and second surface regions. The first surface region **127** corresponds to regions of the non-patterned fluoropolymer **133** where the photosensitive polymer was removed. The second surface region **128** corresponds to the patterned layer **122.** In the embodiment, the photosensitive polymer is a negative type photoresist and
25 unexposed areas are removed in the first developing agent. In other embodiments, the photosensitive polymer may be a positive type photoresist and exposed areas are removed in the developing agent. In some embodiments described in more detail layer, the photosensitive polymer **132** is a photosensitive fluoropolymer and the undercut developing agent includes a mixture of solvents including at least one hydrofluoroether
30 or a perfluorinated solvent.

In FIG. 5D, patterned precursor structure **126** may be contacted with an undercut developing agent comprising a hydrofluoroether or a perfluorinated solvent. The patterned layer **122** has low solubility in the undercut developing agent. In later process steps, patterned layer **122** may also have relatively low solubility in rinse

agents or lift-off agents, if used. The undercut developing agent removes a portion of the non-patterned fluoropolymer layer **133** in registration with the first surface region, thereby forming patterned fluoropolymer layer **123'** and first patterned fluoropolymer structure **121'** having a first undercut profile. Contacting with the undercut developing
5 agent can be accomplished by methods previously disclosed.

The first patterned fluoropolymer structure **121'** may be contacted with a rinse agent including a perfluorinated solvent to form the desired fluoropolymer resist structure **121** over substrate **110** as already described in FIG. 4. In some embodiments, the undercut profile (e.g., the sidewalls of patterned fluoropolymer layer **123'**) or
10 openings **105** may be modified by the rinse step relative to the first patterned fluoropolymer structure, but most of the formation of the openings and undercut profile occurs in the undercut developer step. The rinse is discussed in more detail later.

Referring again to FIG. 5C, in some embodiments, the patterned layer **122** may be formed by methods other than photopatterning a photosensitive polymer. For
15 example, the patterned layer may be ink-jet deposited, stamped, transferred from a donor sheet or the like. In these embodiments, the material for patterned layer **122** is selected so that it also has relatively low solubility in the undercut developing agent, and if used, it may also have relatively low solubility the rinse agent or the lift-off agent.

20

Solvents

Methods of the present disclosure often utilize highly fluorinated solvents due to their orthogonality. Particularly useful highly fluorinated solvents include perfluorinated solvents and hydrofluoroethers (HFEs).

25

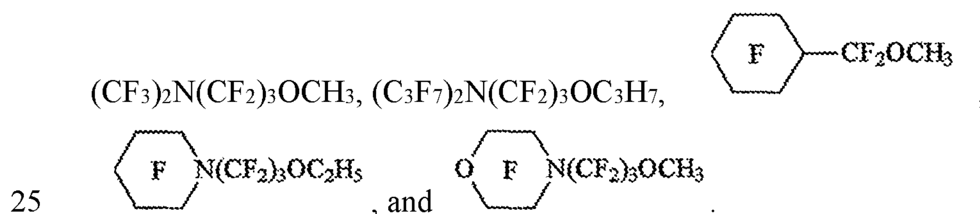
HFE Solvents

There are two main varieties of HFEs useful in the present disclosure: (a) segregated hydrofluoroethers, wherein ether-bonded segments (e.g. alkyl or alkenyl segments) of the HFE are either perfluorinated (e.g., a perfluorocarbon segment) or
30 non-fluorinated (e.g., a hydrocarbon segment), but not partially fluorinated; and (b) non-segregated HFEs, wherein one or both ether-bonded segments are partially fluorinated. In some embodiments, the segments do not include any double bonds (i.e., they are saturated). In some embodiments, the segments may have one or more double or triple bonds. HFEs may have a fluorine content that is at least 50% by weight,

preferably at least 60% by weight, in order to properly solubilize the fluoropolymer(s) of the present disclosure. Some HFEs may have multiple ether units or include saturated nitrogen atoms.

Examples of readily available HFEs and isomeric mixtures of HFEs include, but are not limited to, 1-methoxyheptafluoropropane (HFE-7000 aka Novec™ 7000), an isomeric mixture of methyl nonafluorobutyl ether and methyl nonafluoroisobutyl ether (HFE-7100 aka Novec™ 7100), an isomeric mixture of ethyl nonafluorobutyl ether and ethyl nonafluoroisobutyl ether (HFE-7200 aka Novec™ 7200), 3-ethoxy-l, 1,1,2,3,4,4,5,5,6,6,6-dodecafluoro-2-trifluoromethyl-hexane (HFE-7500 aka Novec™ 7500), 1,1,1,2,3,3-hexafluoro-4-(1,1,2,3,3,3,-hexafluoropropoxy)-pentane (HFE-7600 aka PF7600 (from 3M)), 1-methoxyheptafluoropropane (HFE-7000), 1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-trifluoromethylpentane (HFE-7300 aka Novec™ 7300), 1,2-(1,1,2,2-tetrafluoroethoxy)ethane (HFE-578E), 1,1,2,2-tetrafluoroethyl-1H,1H,5H-octafluoropentyl ether (HFE-6512), 1,1,2,2-tetrafluoroethyl-2,2,2-trifluoroethyl ether (HFE-347E), 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (HFE-458E), 2,3,3,4,4-pentafluorotetrahydro-5-methoxy-2,5-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-furan (HFE-7700 aka Novec™ 7700), 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorooctane-propyl ether (TE6O-C3) and (2E)-1,1,2,3,4,4,5,5,6,6,7,7,7-tridecafluoro-1-methoxy-2-heptene (aka Opteon SF10).

In the above list, segregated HFEs include HFE-7100, HFE-7200, HFE-7300, HFE-7500, HFE-7700 and Opteon SF10. Some additional, non-limiting examples of segregated HFEs include $F(CF_2)_5OCH_3$, $F(CF_2)_6OCH_3$, $F(CF_2)_7OCH_3$, $F(CF_2)_8OCH_2CH_2CH_3$, $F(CF_2)_2O(CF_2)_4OCH_2CH_3$, $F(CF_2)_3OCF(CF_3)CF_2OCH_3$, $(CF_3)_2N(CF_2)_3OCH_3$, $(C_3F_7)_2N(CF_2)_3OC_3H_7$,




Mixtures of HFE solvents may optionally be used. Boiling points of HFEs in the present disclosure typically range from about 30 °C to 200 °C.

Perfluorinated Solvents

Although not limited, it has been presently found that there are at least three primary classes of perfluorinated solvents useful in certain embodiments of the present disclosure including: (a) perfluorocarbons such as perfluoroalkanes; (b) perfluoroalkyl

ethers; and (c) perfluoroalkylamines, any of which may optionally have a cyclic structure. Some non-limiting examples of perfluorocarbons include perfluoro-octane, perfluoro-2-methlypentane, perfluoro-1,3-dimethylcyclohexane and perfluorodecalin. Some non-limiting examples of a perfluoroalkylamines include perfluorotributylamine, perfluorotriethylamine, perfluorotripentylamine. Numerous Fluorinert™ perfluorinated solvents are available from 3M. In some embodiments, perfluorinated solvents of the present disclosure are non-aromatic or saturated compounds. Some non-limiting examples of perfluoroalkyl ethers include Galden® perfluoropolyethers available from Solvay. Boiling points typically range from about 30 °C to 200 °C, alternatively about 50 °C to 200 °C.\

Rinse Agent

According to some embodiments of the present disclosure, a first patterned fluoropolymer structure formed by contact with the undercut developing agent is treated by contact with a rinse agent that includes one or more fluorinated rinse solvents.

In some embodiments, a fluorinated rinse solvent may be a perfluorinated solvent, including but not limited to a perfluoroalkane, a perfluoroalkyl ether, or a perfluoroalkylamine. In some embodiments, a fluorinated rinse solvent may be a hydrofluoroether. In some embodiments, the rinse agent includes two or more independently selected fluorinated rinse solvents. In some embodiments, the rinse agent may include additional rinse compounds (in addition to the one or more fluorinated rinse solvents). For example, the additional rinse compound may include a non-fluorinated or partially fluorinated alcohol, such as 2,2,3,3,4,4,5,5-octafluoro-1-pentanol. In some embodiments, the additional rinse compounds may aid in reducing unwanted fluoropolymer residue. In some embodiments, the one or more fluorinated solvents may collectively constitute at least 50 % by weight of the rinse agent, alternatively at least 80 %, alternatively at least 90 %, alternatively at least 95 %, alternatively at least 99 %. In some embodiments, the one or more fluorinated solvents may collectively constitute at least 50 % of the volume of the rinse agent, alternatively at least 80 %, alternatively at least 90 %, alternatively at least 95 %, alternatively at least 99 %.

In an embodiment, the rinse agent is contacted with the first patterned fluoropolymer structure in the presence of some undercut developing agent. That is, in such embodiments, the undercut developing agent is not first removed or dried, but rather, the rinse agent acts to dilute and wash away the undercut developing agent.

5 It has been unexpectedly found that certain rinse agents, while they may not quickly dissolve the fluoropolymer layer, can nevertheless facilely remove fluoropolymer material dissolved in the undercut developer agent. This serves to shut down continued development and undercut formation, with concurrent removal of dissolved fluoropolymer material to reduce unwanted re-precipitation or residue in the

10 exposed surface portion of the device substrate. In some embodiments, some of the dissolved fluoropolymer material may eventually begin to precipitate, but in a time frame after the dissolved fluoropolymer has been removed from the area near the device substrate surface. In some embodiments, the dissolved fluoropolymer material stays solubilized or dispersed in the rinse agent.

15 The dissolution rate of a fluoropolymer layer, e.g., fluoropolymer layer **133**, unexposed portions of fluorinated photopolymer layer **115** and patterned fluorinated photopolymer **118L**, may be lower in the rinse agent than in the undercut developing agent. Development rate measurements may be performed under temperature conditions that approximate the actual conditions used when forming the fluoropolymer

20 structures. In one method, a fluoropolymer layer thickness is measured in a dry state. The fluoropolymer is then contacted with a solvent for a period of time under the appropriate conditions, the solvent is then removed after the period of time (e.g., by spin drying on a conventional wafer spinner) and the fluoropolymer layer thickness is remeasured. The loss in thickness over time corresponds to a dissolution rate.

25 In some embodiments, the undercut developing agent and the rinse agent are used at approximately the same temperature, i.e., within about 2 °C, such same temperature falling within a range of about 15 °C to 35 °C, alternatively about 20 °C to 30 °C. In such embodiments, dissolution rate differences may be controlled largely by selection of the solvents used in the undercut developing agent and rinse agent.

30 In some embodiments, the rinse agent is provided at a temperature that is lower than the temperature of the undercut developing agent. In some embodiments, the rinse agent temperature is at least 5 °C cooler than the undercut developing agent temperature, alternatively at least 10 °C cooler, alternatively at least 15 °C cooler,

alternatively at least 20 °C cooler. In such embodiments, dissolution rate differences between the undercut developing agent and rinse agent may be controlled in part by temperature and in part by composition (if different).

In some embodiments, the fluoropolymer layer has a dissolution rate in the
5 undercut developing agent that is at least 3 times greater than the dissolution rate of the fluoropolymer in the rinse agent, alternatively at least 5 times greater, alternatively at least 10 times greater. In some embodiments, the fluoropolymer layer has a dissolution rate in the rinse agent that is less than about 5 nm/sec, alternatively less than about 2 nm/sec. In some embodiments, a fluoropolymer layer has a dissolution rate in the
10 undercut developing agent that is at least 6 nm/sec, alternatively at least 10 nm/sec.

In some embodiments, a fluorinated rinse solvent of the rinse agent is a perfluoroalkyl ether. For example, the rinse agent may include a perfluorinated polyether solvent sold under the Galden® brand, including but not limited to, as Galden HT-110, HT-135 and HT-170.

15 In some embodiments, a fluorinated rinse solvent of the rinse agent is a perfluorinated alkane or a perfluorinated tri-N-alkyl amine. For example, the rinse agent may include a perfluorinated solvent such as perfluorodecalin, Fluorinert FC 40 (3M) or CT-Solv-180 (Asahi Glass).

In some embodiments, a fluorinated rinse solvent of the rinse agent is a
20 hydrofluoroether. For example, the rinse agent may include a hydrofluoroether such as HFE-7300, HFE-7200, HFE-7100 or HFE-7000.

In some embodiments, the rinse agent (or the highest boiling component thereof) has a boiling point lower than the boiling point of the undercut developing agent (or the highest boiling component thereof). In some embodiments, the rinse agent
25 (or highest boiling component thereof) has a boiling point of about 135 °C or lower, alternatively about 110 °C or lower, alternatively about 100 °C or lower, alternatively about 80 °C or lower, alternatively about 70 °C or lower.

In some embodiments, the rinse agent has a kinematic viscosity lower than a kinematic viscosity of the undercut developing agent. In some embodiments, the rinse
30 agent has a kinematic viscosity of about 2.0 centistokes or less, alternatively about 1.8 centistokes or less, alternatively about 1.5 centistokes or less.

In some embodiments, the fluoropolymer (e.g., the first patterned fluoropolymer structure) may be contacted with the rinse agent for a period of time of about 60

seconds or less, alternatively 30 seconds or less, alternatively 15 seconds or less. In some embodiments, the rinse agent contact time is in a range of 1 seconds to 60 seconds, alternatively in a range of about 2 seconds to 30 seconds, alternatively in a range of 3 seconds to 15 seconds. In some embodiments, contact time with the rinse agent is lower than the contact time in the undercut developing agent. In some embodiments, the composition or temperature of the rinse agent may be changed during the contact period. For example, the rinse agent may have a first rinse composition when initially contacted with the fluoropolymer. At some later time during contact the rinse is changed to have a second rinse composition that is different from the first. The second rinse composition may have a lower boiling point than the first rinse composition. With respect to the fluoropolymer layer, the second rinse composition may have a lower dissolution rate than the first rinse composition. In some embodiments, the rinse agent composition may be changed multiple times during contact. In some embodiments, the rinse agent composition may be changed gradually during contact, e.g., in a gradient fashion.

Contacting with the rinse agent can be accomplished by immersion into the rinse agent or by coating the rinse agent in some way, e.g., by spin coating, slot die coating or spray coating.

After treatment with the rinse agent, the fluorinated structure is typically dried. The drying step may optionally include a fan, a gas knife, spin drying, application of heat or IR radiation, application of vacuum, some combination or other methods known in the art.

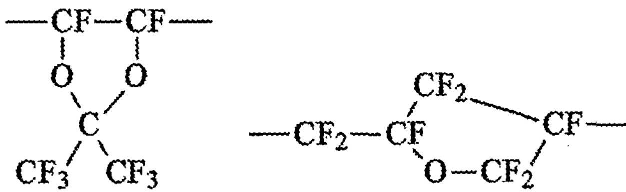
Fluoropolymer Materials and Methods

Some non-limiting methods and materials for preparing a fluoropolymer structure having an undercut profile according to some embodiments of FIG. 4 and 5 are described below in more detail where the patterned layer **122** is a fluoropolymer, for example formed from a photosensitive fluoropolymer. The fluoropolymer resist structures of the present disclosure may also be referred to herein as patterned resist structures. In some embodiments, the resist structures have at least a first fluoropolymer layer (e.g. patterned fluoropolymer layer **123**, provided from non-patterned fluoropolymer layer **133**) and a second fluoropolymer layer (e.g. as a fluorinated patterned layer **122**, optionally provided from layer a fluorinated photosensitive polymer **132**) provided over the first fluoropolymer layer. In some embodiments, the

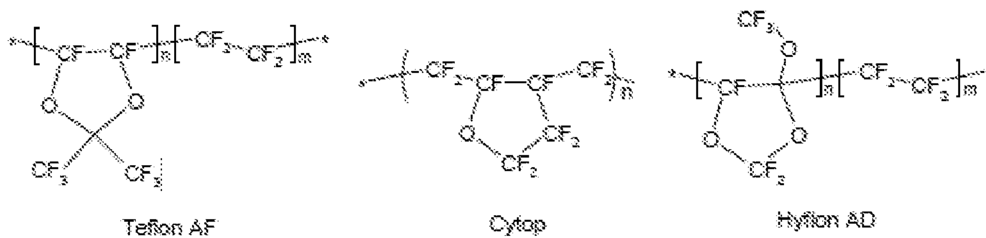
second fluoropolymer layer has a lower fluorine content than the first fluoropolymer layer.

First Fluoropolymer Layer

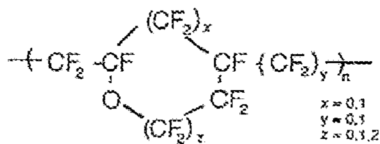
5 In some embodiments, the first fluoropolymer layer includes a first fluoropolymer material that is a highly fluorinated molecular solid or polymer (both are referred to herein as a fluoropolymer). The first fluoropolymer may have a total fluorine content in a range of 50 to 75% by weight. In some embodiments, the first fluoropolymer material is perfluorinated. In an embodiment, the first fluoropolymer 10 material includes a fluorinated cyclic structure. In an embodiment, the first fluoropolymer material includes a perfluorinated cyclic ether or dioxol. Some non-limiting examples of the first fluoropolymer materials include those having repeating units such as




, and similar materials. In some 15 embodiments, the cyclic portion may be a copolymer with tetrafluoroethylene-based repeating units or similar materials. Preferably, the first fluoropolymer material is mostly amorphous in nature. Examples of commercially available materials useful as the first fluoropolymer material include Cytop, Teflon AF and Hyflon AD.




20 A more generic structure for Cytop-class materials includes

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The term “perfluorinated polymers” as used herein includes polymers that are otherwise perfluorinated, but that may include small amounts of non-perfluorinated

impurities or terminal groups that may be functionalized in some way with a non-perfluorinated group.

First fluoropolymer materials are often soluble in highly fluorinated solvents, especially perfluorinated solvents. Some non-limiting examples include perfluorodecalin, Fluorinert FC 40 (3M) and CT-Solv-180 (Asahi Glass). They may also be substantially soluble in a first-type of HFE solvent, but often not a second-type. In an embodiment, the first fluoropolymer material is selected to be soluble in first-type of HFE that is a saturated HFE having at least four more perfluorinated carbon atoms than hydrogen-containing carbon atoms. A carbon atom is perfluorinated if, aside from any bonds to other carbon, oxygen or nitrogen atoms, its valency is completed with one or more fluorine atoms instead of hydrogen. In an embodiment, the first fluoropolymer material is soluble in a first-type of HFE that is a saturated, segregated hydrofluoroether having at least five perfluorinated carbon atoms and less than three hydrogen-containing carbon atoms. Some non-limiting examples of such “first-type” HFE solvents include HFE-7300, HFE-7500 and HFE-7700.

Some example solvents that do not meet the “first-type” criteria include HFE-7100, HFE-7200, HFE-7600 and HFE-6512. In some embodiments the first fluoropolymer material may be substantially less soluble in such solvents compared the first-type of HFE solvents defined above. By “substantially less soluble”, it is meant herein that, when measured at about 20 °C, the rate of dissolution of a layer of a polymer material in a solvent is 1/2 or less, alternatively 1/5 or less than the rate in another solvent in which the polymer is substantially soluble. In the context of this paragraph “substantially soluble”, it is meant that a layer of a polymer material has a dissolution rate in a solvent that is at least about 2 nm/sec. In an embodiment, the dissolution rate of a first fluoropolymer material is at least 2 nm/sec or higher in a perfluorinated solvent or a first-type of HFE, but 1 nm/sec or lower in other HFE solvents. In some cases, a first fluoropolymer may not have facile dissolution kinetics in a solvent and fail to be classified as “substantially soluble”, but may still be “substantially thermodynamically soluble” meaning that the solvent can dissolve and hold in solution at least 1% by weight of the first fluoropolymer material (even though such dissolution may take a long time).

Second Fluoropolymer Layer

The second fluoropolymer layer includes a second fluoropolymer material that may have a fluorine content (by weight) less than that of the first fluoropolymer material. In an embodiment, the fluorine content is at least 15% by weight, alternatively at least 25% by weight, alternatively at least 35% by weight, or alternatively at least 45% by weight.

In some embodiments, the second fluoropolymer material is a copolymer comprising at least two distinct repeating units including a first repeating unit having a fluorine-containing group and a second repeating unit having a functional group. Incorporation of functional groups other than fluorine-containing groups can be helpful to tailor the solubility of the fluorinated material and may also improve the coatability of compositions comprising the fluorinated copolymer over a device substrate and the coatability of layers that may be provided over the second fluorinated material layer. In some embodiments, the functional group may be a solubility-altering reactive group that provides photosensitivity. If patterned layer **122** is provided by printing rather than photopatterning, the second fluoropolymer material does not necessarily require a solubility-altering reactive group.

In an embodiment, one or more of the repeating units of the copolymer may be formed via a post-polymerization reaction. In this embodiment, an intermediate polymer (a precursor to the desired copolymer) is first prepared, said intermediate polymer comprising suitably reactive functional groups for forming one of more of the specified repeat units. For example, an intermediate polymer containing pendant carboxylic acid moieties can be reacted with a fluorinated alcohol compound in an esterification reaction to produce the specified fluorinated repeating unit. Similarly, a precursor polymer containing an alcohol can be reacted with a suitably derivatized aliphatic hydrocarbon group to form an aliphatic hydrocarbon functional groups. In another example, a polymer containing a suitable leaving group such as primary halide can be reacted with an appropriate compound bearing a phenol moiety to form the desired repeat unit via an etherification reaction. In addition to simple condensation reactions such as esterification and amidation, and simple displacement reactions such as etherification, a variety of other covalent-bond forming reactions well-known to practitioners skilled in the art of organic synthesis can be used to form any of the specified repeat units. Examples include palladium-catalyzed coupling reactions,

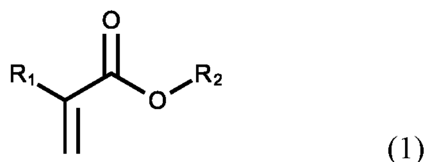
"click" reactions, addition to multiple bond reactions, Wittig reactions, reactions of acid halides with suitable nucleophiles, and the like.

In some embodiments, the repeating units are formed by polymerization of the appropriate monomers each having a polymerizable group, rather than by attachment to an intermediate polymer. The polymerizable group may, for example, be polymerized by step-growth polymerization using appropriate functional groups or by a chain polymerization such as radical polymerization. Some non-limiting examples of useful radical polymerizable groups include acrylates (e.g. acrylate, methacrylate, cyanoacrylate and the like), acrylamides, vinylenes (e.g., styrenes), vinyl ethers and vinyl esters. Although many of the embodiments below refer to polymerizable monomers, analogous structures and ranges are contemplated and within the scope of the present disclosure wherein one or more of the repeating units are formed instead by attachment to an intermediate polymer, by polymerization or other means.

In an embodiment, the second fluorinated material includes a copolymer formed at least from a first monomer having a fluorine-containing group and a second monomer having a functional group.

The fluorine-containing group of the first monomer or the first repeating unit is preferably an alkyl or aryl group that may optionally be further substituted with chemical moieties other than fluorine, e.g., chlorine, a cyano group, or a substituted or unsubstituted alkyl, alkoxy, alkylthio, aryl, aryloxy, amino, alkanoate, benzoate, alkyl ester, aryl ester, alkanone, sulfonamide or monovalent heterocyclic group, or any other substituent that a skilled worker would readily contemplate that would not adversely affect the performance of the fluorinated polymer. Throughout this disclosure, unless otherwise specified, any use of the term alkyl includes straight-chain, branched and cyclo alkyls. In an embodiment, the first monomer does not contain protic or charged substituents, such as hydroxy, carboxylic acid, sulfonic acid or the like.

In an embodiment, the first monomer has a structure according to formula (1):




(1)

In formula (1), $R_1$ represents a hydrogen atom, a cyano group, a methyl group or an ethyl group. $R_2$ represents a fluorine-containing group, for example, a substituted or unsubstituted alkyl group having at least 5 fluorine atoms, alternatively at least 10

fluorine atoms. In an embodiment, the alkyl group is a hydrofluorocarbon or hydrofluoroether having at least as many fluorine atoms as carbon atoms. In an embodiment $R_2$ represents a perfluorinated alkyl or a 1H,1H,2H,2H-perfluorinated alkyl having at least 4 carbon atoms. Examples of the latter may include
5 1H,1H,2H,2H-perfluorooctyl (aka 2-perfluorohexyl ethyl). Examples of a first monomers include 1H,1H,2H,2H-perfluorooctyl methacrylate ("FOMA") and similar materials.

Some non-limiting examples of polymerizable monomers having a fluorine-containing group include the following:

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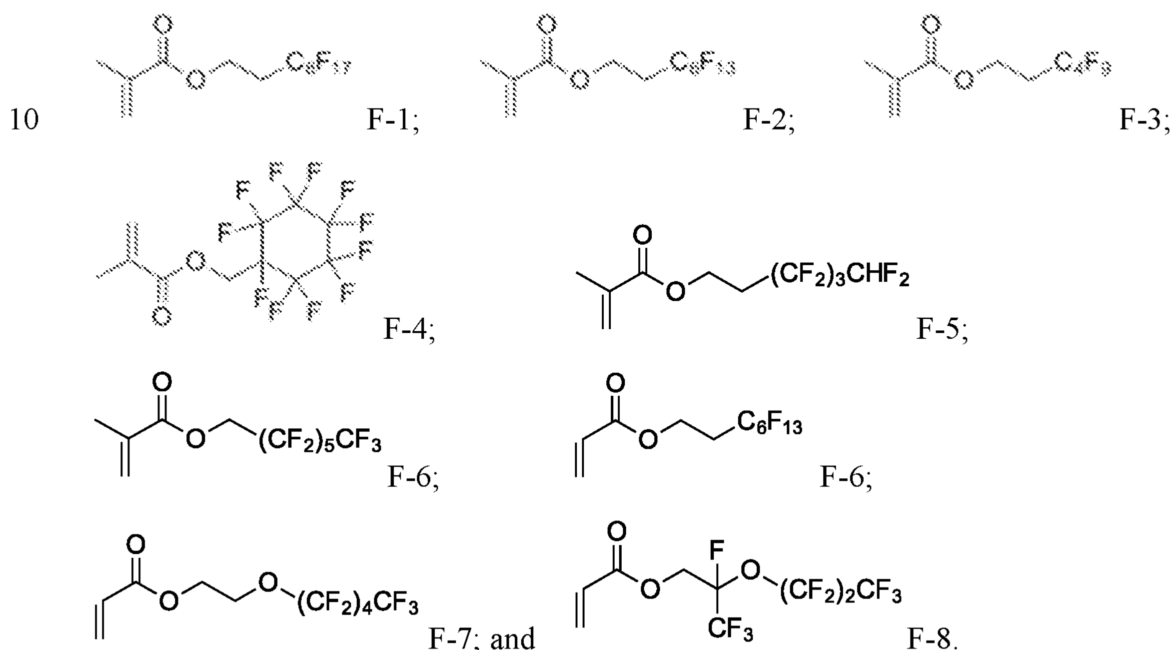
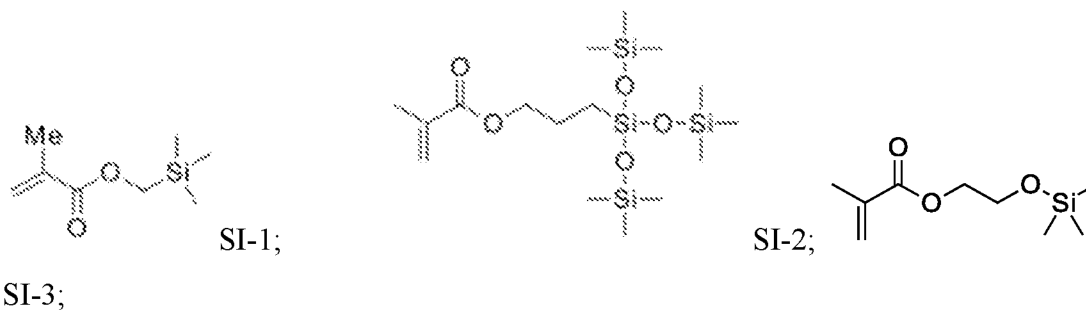


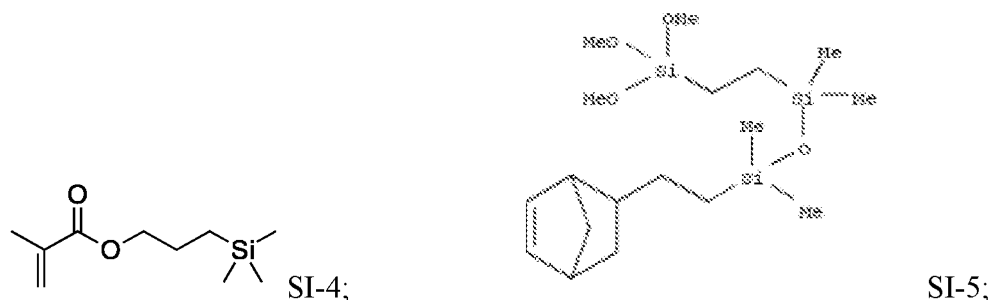

15 Multiple "first repeating units" or "first monomers" may be used in the copolymer, i.e., the copolymer may include more than just one type of fluorine-containing group or fluorine-containing first monomer.

The second monomer is one capable of being copolymerized with the first monomer. The second monomer includes a polymerizable group and a functional
20 group as described below. In some embodiments, functional groups do not include substantial amounts of fluorine substituents, i.e., they generally include three fluorine atoms or fewer. In some embodiments, the functional groups are not fluorinated.

In an embodiment, the functional group includes a silane or siloxane. Some non-limiting examples of polymerizable monomers incorporating such functional
25 groups are shown below:

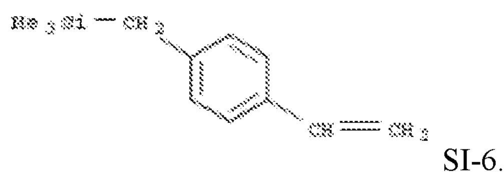


SI-1; SI-2; SI-3;



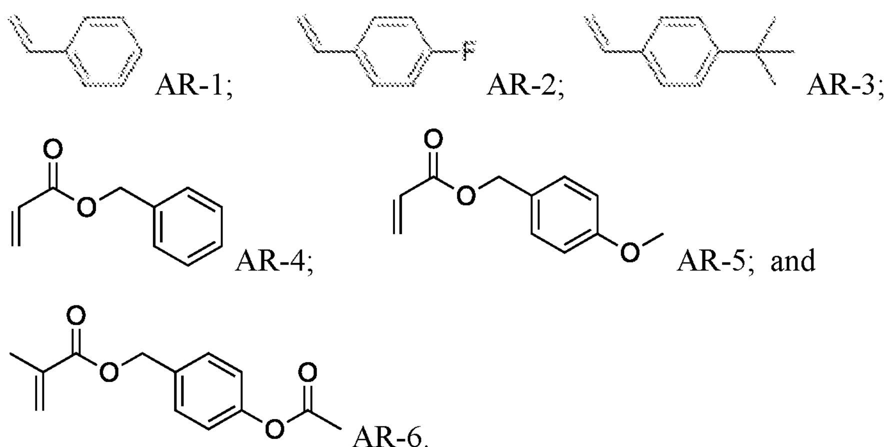
SI-4; SI-5;

and



SI-6.

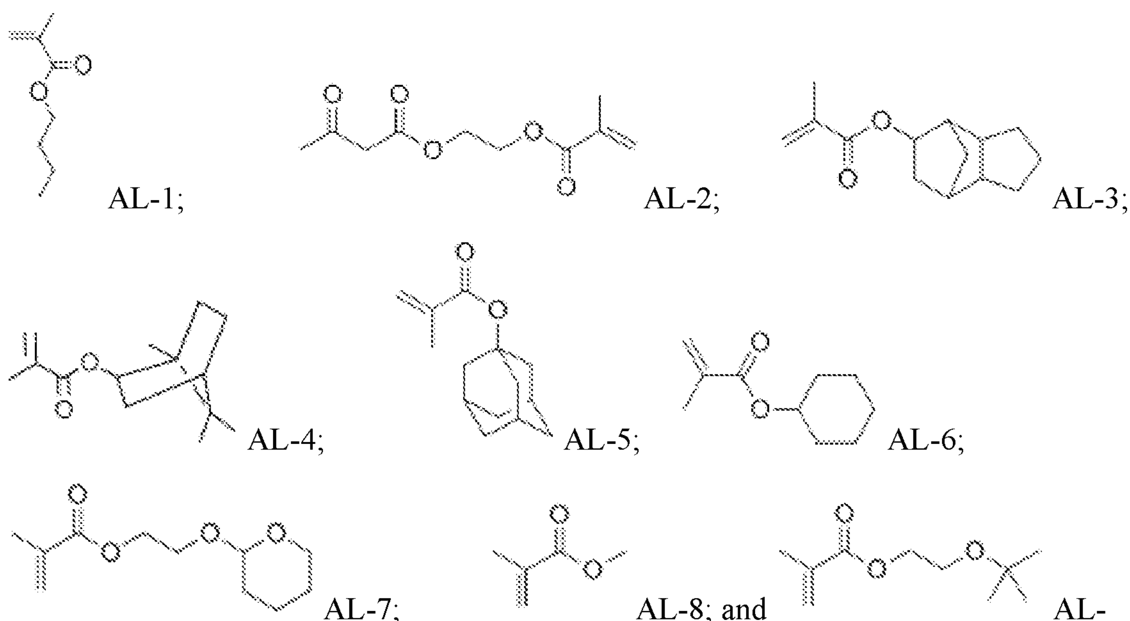
In an embodiment, the functional group includes an aromatic hydrocarbon that does not include a protic substituent, but may optionally include an alkyl group, an ether group, an ester groups or a ketone group. Some examples of polymerizable monomers incorporating such functional groups are shown below:



AR-1; AR-2; AR-3; AR-4; AR-5; and AR-6.

In an embodiment, the functional group includes a cyclic or non-cyclic aliphatic hydrocarbon that does not include a protic substituent. The aliphatic hydrocarbon functional group may optionally include non-protic substituents including, but not

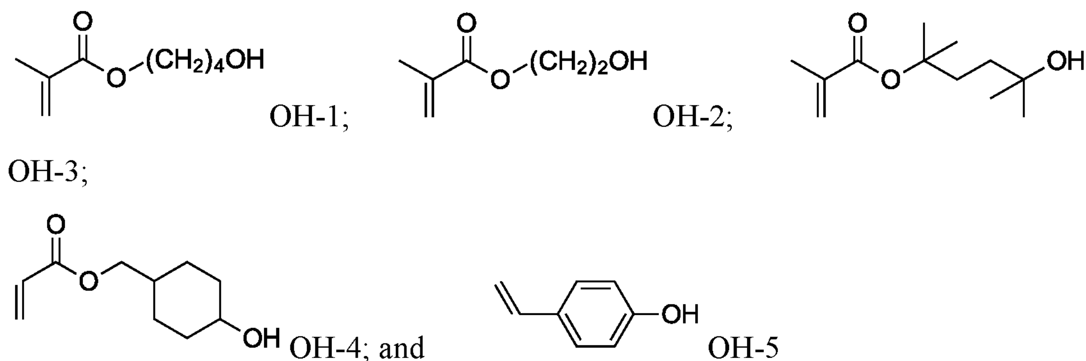
limited to, ether groups, ester groups, and ketone groups. In an embodiment, the aliphatic hydrocarbon functional group does not include any fluorine substituents. In an embodiment, the copolymer comprising an aliphatic hydrocarbon functional group has a total fluorine content in a range of 46 to 53% by weight. Some non-limiting
5 examples of polymerizable monomers incorporating such functional groups are shown below:



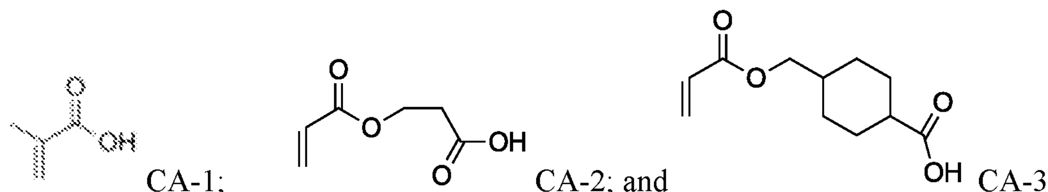

10 9.

In an embodiment, the functional group includes a protic substituent including, but not limited to alcohol groups, carboxylic acid groups, primary or secondary amine groups, and sulfonic acid groups. In an embodiment, when a functional group includes a protic substituent the copolymer has a total fluorine content of more than 50% by
15 weight.

In an embodiment, the functional group is an alcohol group and the copolymer has a total fluorine content of at least 55% by weight. Alternatively, or in addition, the functional group is an alcohol group and the copolymer has a total hydroxyl group content of less than 1.0% by weight, preferably less than 0.5% by weight. Hydroxyl
20 group content refers to the mass of OH substituents of the alcohol (each having a formula weight of 17 daltons) relative to total mass of the copolymer. Some non-limiting examples of polymerizable monomers incorporating such functional groups are shown below:




In an embodiment, the functional group is carboxylic acid group and the copolymer has a total fluorine content of at least 56% by weight. Alternatively, or in addition, the functional group is a carboxylic acid group and the copolymer has a total hydroxyl group content of less than 0.5% by weight, preferably less than 0.25% by weight. Hydroxyl group content refers to the mass of OH portion of the carboxylic acid substituents (each having a formula weight of 17 daltons) relative to total mass of the copolymer. Some non-limiting examples of polymerizable monomers incorporating such functional groups are shown below:




Photosensitive Fluoropolymer

As mentioned, photosensitive fluoropolymers (fluorinated photopolymers) may be used as the second fluoropolymer layer, e.g., to prepare layer **122**. The following description is also generally applicable to layer **111** described above with respect to single layer embodiments. Photosensitive fluoropolymers can be provided, e.g., by coating a photosensitive fluoropolymer composition (also referred to as a fluorinated photopolymer composition) that includes a fluorinated solvent (e.g., a hydrofluoroether), a fluorinated photopolymer material, and optionally additional materials such as sensitizing dyes, photo-acid generator compounds, stabilizers, quenchers and the like. In an embodiment, the fluorinated photopolymer material includes a copolymer formed at least from a first monomer having a fluorine-containing group and a second monomer having a solubility-altering reactive group as the

functional group. Additional monomers may optionally be incorporated into the copolymer. The first monomer is one capable of being copolymerized with the second monomer and has at least one fluorine-containing group. Useful embodiments for the first monomer in a fluorinated photopolymer are essentially the same as those already 5 been described above with respect to the first monomer of the second fluoropolymer material. In some embodiments the fluorinated photopolymer has a total fluorine content of at least at least 15%. In an embodiment, the total fluorine content is in a range of 15% to 60%, alternatively 30 to 60%, or alternatively 35 to 55%.

The photosensitive fluoropolymer may suitably be a random copolymer, but 10 other copolymer types may be used, e.g., block copolymers, alternating copolymers, and periodic copolymers. The term “repeating unit” herein is used broadly herein and simply means that there is more than one unit. The term is not intended to convey that there is necessarily any particular order or structure with respect to the other repeating units unless specified otherwise. When a repeating unit represents a low mole % of the 15 combined repeating units, there may be only one such unit on a polymer chain. The fluoropolymer may be optionally blended with one or more other polymers, preferably other fluorine-containing polymers. The fluoropolymer may optionally be branched, which may in certain embodiments enable lower fluorine content, faster development and stripping rates, or incorporation of groups that otherwise may have low solubility in 20 a fluorinated polymer. In some embodiments, the photosensitive fluoropolymer does not include any branching units (1 mol% or less). In some cases, this can further reduce its solubility in the undercut developing agent and improve overall yield.

As previously mentioned, the specified repeating units may be formed via a post-polymerization reaction or alternatively via direct polymerization of two (or more) 25 appropriate monomers, rather than by attachment to an intermediate polymer. Although many of the embodiments below refer to polymerizable monomers, analogous structures and ranges are contemplated wherein one or more of the first and second repeating units are formed by attachment of the relevant group to an intermediate polymer as described above.

30 The second monomer for the fluorinated photopolymer is one capable of being copolymerized with the first monomer. The second monomer includes a polymerizable group and a solubility-altering reactive group. Some non-limiting examples of useful polymerizable groups include those described for the first monomer.

In some embodiments, the solubility-altering reactive group of the second monomer or second repeating unit is an acid-forming precursor group. Upon exposure to light, the acid-forming precursor group generates a polymer-bound acid group, e.g., a carboxylic or sulfonic acid. This may drastically change its solubility relative to the unexposed regions thereby allowing development of an image with the appropriate solvent. In an embodiment, the developing agent includes a fluorinated solvent that selectively dissolves unexposed areas. In an embodiment, a carboxylic acid-forming precursor is provided from a monomer in a weight percentage range of 4 to 40% relative to the copolymer, or alternatively in a weight percentage range of 10 to 30%.

One class of acid-forming precursor groups includes the non-chemically amplified type (e.g., non-acid catalyzed). An example of a second monomer with such a group is 2-nitrobenzyl methacrylate. The non-chemically amplified precursor group may directly absorb light to initiate de-protection of the acid-forming groups. Alternatively, a sensitizing dye may be added to the composition whereby the sensitizing dye absorbs light and forms an excited state capable of directly sensitizing or otherwise initiating the de-protection of acid-forming precursor groups. The sensitizing dye may be added as a small molecule or it may be attached or otherwise incorporated as part of the copolymer. Unlike chemically amplified formulations that rely on generation of an acid (see below), non-chemically amplified photopolymers may sometimes be preferred when a photopolymer is used on or near an acid-sensitive or acid-containing material.

A second class of acid-forming precursor groups includes the chemically amplified type. This typically requires addition of a photo-based generator or a photo-acid generator (PAG) to the photopolymer composition, e.g., as a small molecule additive to the solution. The PAG may function by directly absorbing radiation (e.g. UV light) to cause decomposition of the PAG and release an acid. Alternatively, a sensitizing dye may be added to the composition whereby the sensitizing dye absorbs radiation and forms an excited state capable of reacting with a PAG to generate an acid. The sensitizing dye may be added as a small molecule incorporated as part of the copolymer. In an embodiment, the sensitizing dye (either small molecule or attached) is fluorinated. In an embodiment, the sensitizing dye may be provided in a range of 0.5 to 10 % by weight relative to the total copolymer weight. The photochemically generated acid catalyzes the de-protection of acid-labile protecting groups of the acid-forming precursor. In some embodiments, chemically amplified photopolymers can be

particularly desirable since they enable the exposing step to be performed through the application of relatively low energy UV light exposure. This is advantageous since some active organic materials useful in applications to which the present disclosure pertains may decompose in the presence of UV light, and therefore, reduction of the
5 energy during this step permits the photopolymer to be exposed without causing significant photolytic damage to underlying active organic layers. Also, reduced light exposure times improve the manufacturing throughput of the desired devices.

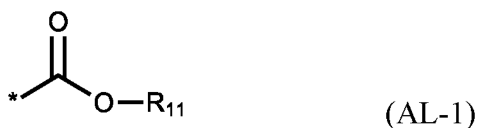
Examples of acid-forming precursor groups that yield a carboxylic acid include, but are not limited to: A) esters capable of forming, or rearranging to, a tertiary cation,
10 e.g., t-butyl ester, t-amyl ester, 2-methyl-2-adamantyl ester, 1-ethylcyclopentyl ester, and 1-ethylcyclohexyl ester; B) esters of lactone, e.g., γ-butyrolactone-3-yl, γ-butyrolactone-2-yl, mevalonic lactone, 3-methyl-γ-butyrolactone-3-yl, 3-tetrahydrofuranyl, and 3-oxocyclohexyl; C) acetal esters, e.g., 2-tetrahydropyranyl, 2-tetrahydrofuranyl, and 2,3-propylenecarbonate-1-yl; D) beta-cyclic ketone esters, E)
15 alpha-cyclic ether esters; and F) MEEMA (methoxy ethoxy ethyl methacrylate) and other esters which are easily hydrolyzable because of anchimeric assistance. In an embodiment, the second monomer comprises an acrylate-based polymerizable group and a tertiary alkyl ester acid-forming precursor group, e.g., t-butyl methacrylate ("TBMA") or 1-ethylcyclopentyl methacrylate ("ECPMA").

20 In an embodiment, the solubility-altering reactive group is an hydroxyl-forming precursor group (also referred to herein as an "alcohol-forming precursor group"). The hydroxyl-forming precursor includes an acid-labile protecting group and the photopolymer composition typically includes a PAG compound and operates as a "chemically amplified" type of system. Upon exposure to light, the PAG generates an
25 acid (either directly or via a sensitizing dye as described above), which in turn, catalyzes the deprotection of the hydroxyl-forming precursor group, thereby forming a polymer-bound alcohol (hydroxyl group). This significantly changes its solubility relative to the unexposed regions thereby allowing development of an image with the appropriate solvent (typically fluorinated). In an embodiment, the developing agent
30 includes a fluorinated solvent that selectively dissolves unexposed areas. In an embodiment, a hydroxyl-forming precursor is provided from a monomer in a weight percentage range of 4 to 40 % relative to the copolymer.

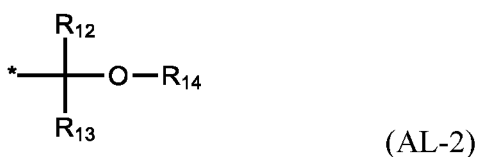
In an embodiment, the hydroxyl-forming precursor has a structure according to formula (2):

(2)

wherein $R_5$ is a carbon atom that forms part of the second repeating unit or second monomer, and $R_{10}$ is an acid-labile protecting group. Non-limiting examples of useful acid-labile protecting groups include those of formula (AL-1), acetal groups of the formula (AL-2), tertiary alkyl groups of the formula (AL-3) and silane groups of the formula (AL-4).



(AL-1)

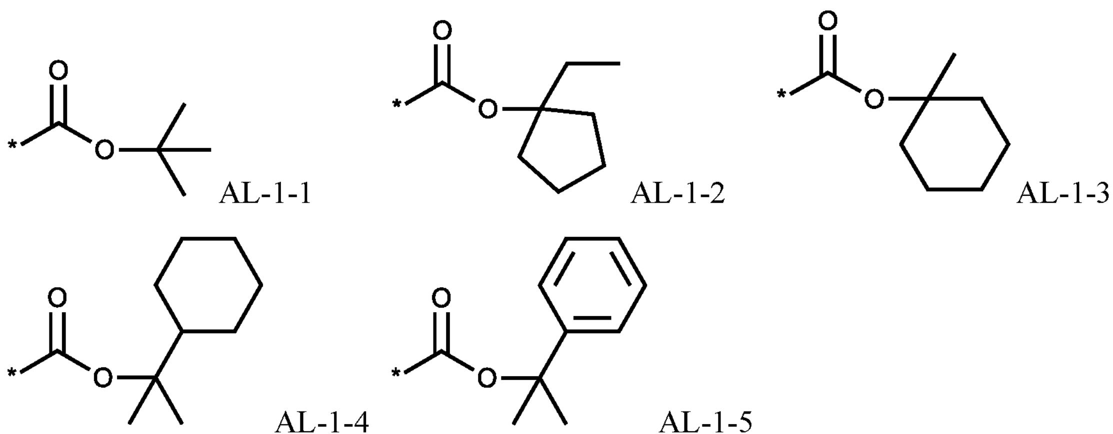


(AL-2)

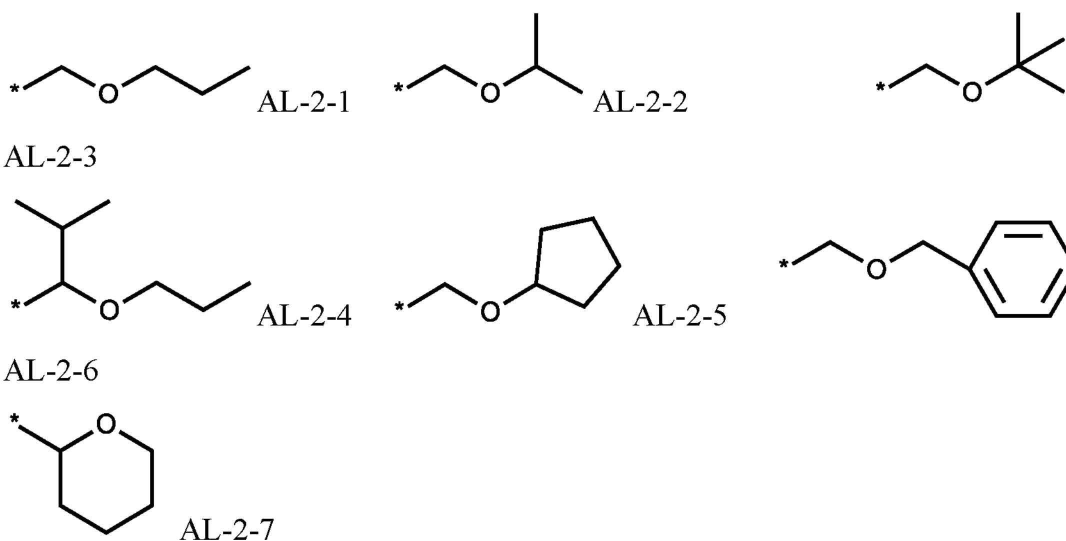
(AL-3)

(AL-4)

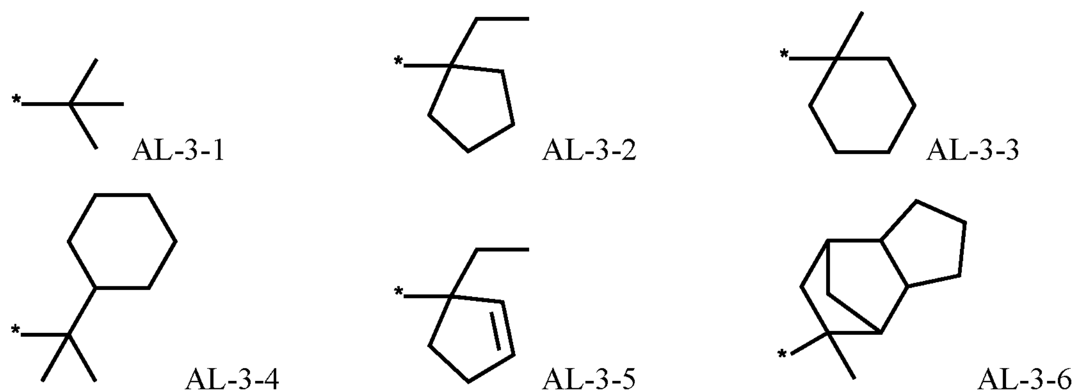
In formula (AL-1), $R_{11}$ is a monovalent hydrocarbon group, typically a straight, branched or cyclic alkyl group, of 1 to 20 carbon atoms that may optionally be substituted with groups that a skilled worker would readily contemplate would not adversely affect the performance of the precursor. In an embodiment, $R_{11}$ may be a tertiary alkyl group. Some representative examples of formula (AL-1) include:



In formula (AL-2), $R_{14}$ is a monovalent hydrocarbon group, typically a straight, branched or cyclic alkyl group, of 1 to 20 carbon atoms that may optionally be substituted. $R_{12}$ and $R_{13}$ are independently selected hydrogen or a monovalent hydrocarbon group, typically a straight, branched or cyclic alkyl group, of 1 to 20 carbon atoms that may optionally be substituted. Some representative examples of formula (AL-2) include:




In formula (AL-3), $R_{15}$, $R_{16}$, and $R_{17}$ represent an independently selected a monovalent hydrocarbon group, typically a straight, branched or cyclic alkyl group, of 1 to 20 carbon atoms that may optionally be substituted. Some representative examples of formula (AL-3) include:

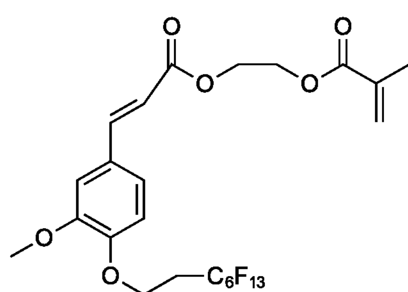



In formula (AL-4), $R_{18}$, $R_{19}$ and $R_{20}$ are independently selected hydrocarbon groups, typically a straight, branched or cyclic alkyl group, of 1 to 20 carbon atoms that may optionally be substituted.

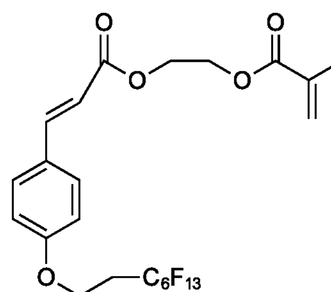
The descriptions of the above acid-labile protecting groups for formulae (AL-2), (AL-3) and (AL-4) have been described in the context of hydroxyl-forming precursors. These same acid-labile protecting groups, when attached instead to a carboxylate

group, may also be used to make some of the acid-forming precursor groups described earlier.

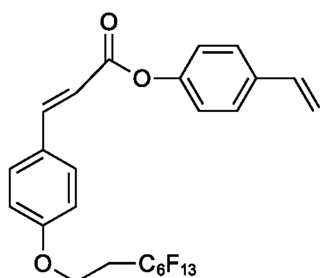
In an embodiment, the solubility-altering reactive group is a cross-linkable group, e.g., an acid-catalyzed cross-linkable group or a photo cross-linkable (non-acid catalyzed) group. Photo cross-linkable groups typically have at least one double bond so that when the group forms an excited state (either by direct absorption of light or by excited state transfer from a sensitizing dye), sets of double bonds from adjacent polymer chains crosslink. In an embodiment, the photo cross-linkable group (not catalyzed) comprises a cinnamate that may optionally further include fluorine-containing substituents. Some non-limiting examples of polymerizable monomers including such cinnamates are shown below:



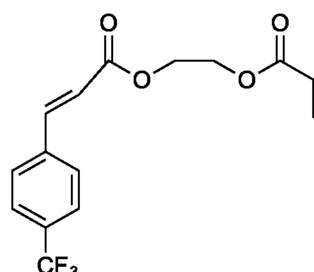
(C-1)



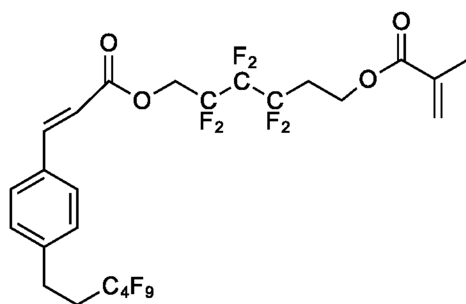
(C-2)



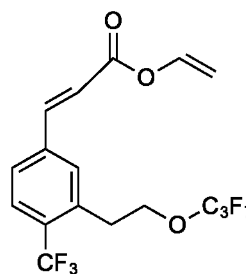
(C-3)



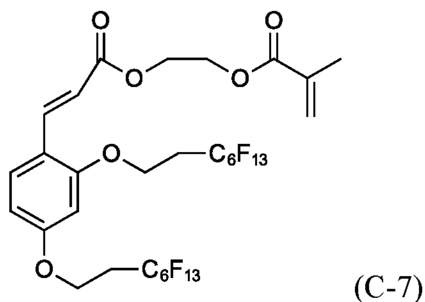
(C-4)



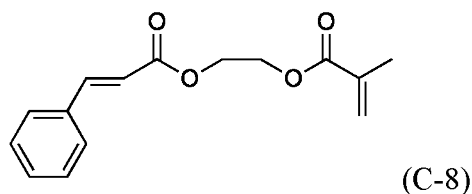
(C-5)



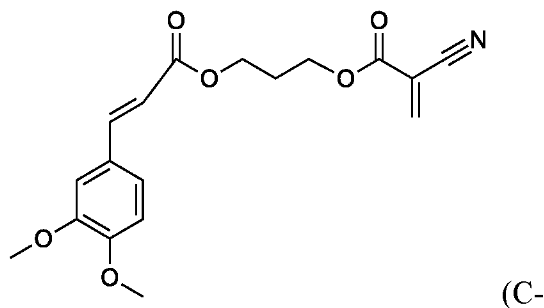
(C-6)




(C-7)




(C-8)



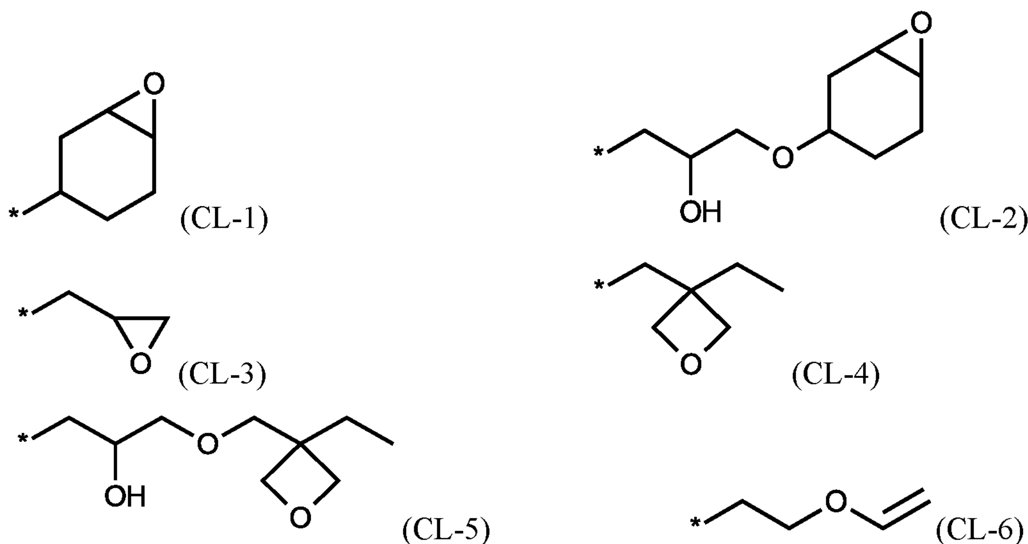

(C-9)

5 Compositions comprising such materials may optionally further include a sensitizing dye. Some non-limiting examples of useful sensitizing dyes for cinnamate cross-linking groups include diaryl ketones (e.g., benzophenones), arylalkyl ketones (e.g., acetophenones), diaryl butadienes, diaryl diketones (e.g. benzils), xanthones, thioxanthones, naphthalenes, anthracenes, benzanthrone, phenanthrenes, crysens,
10 anthrones, 5-nitroacenapthene, 4-nitroaniline, 3-nitrofluorene, 4-nitromethylaniline, 4-nitrobiphenyl, picramide, 4-nitro-2,6-dichlorodimethylaniline, Michler's ketone, N-acyl-4-nitro-1-naphthylamine.

Examples of acid-catalyzed cross-linkable groups include, but are not limited to, cyclic ether groups and vinyloxy groups. In an embodiment, the cyclic ether is an
15 epoxide or an oxetane. The photopolymer composition including an acid-catalyzed cross-linkable group typically includes a PAG compound and operates as a "chemically amplified" type of system in a manner described above. Upon exposure to light, the PAG generates an acid (either directly or via a sensitizing dye as described above), which in turn, catalyzes the cross-linking of the acid-catalyzed cross-linkable groups.
20 This significantly changes its solubility relative to the unexposed regions thereby allowing development of an image with the appropriate fluorinated solvent. Usually, cross-linking reduces solubility. In an embodiment, the developing agent includes a fluorinated solvent that selectively dissolves unexposed areas, e.g., an HFE solvent. In

an embodiment, a cross-linkable group is provided from a monomer in a weight percentage range of 4 to 40 % relative to the copolymer.

Some non-limiting examples of some acid-catalyzed cross-linkable groups include the following wherein (*) refers to an attachment site to the polymer or the
5 polymerizable group of a monomer:




In an embodiment, the solubility-altering reactive groups are ones that, when
10 the photopolymer composition or layer is exposed to light, undergo a bond-breaking reaction to form a material with higher solubility in fluorinated solvents. For example, the solubility-altering reactive groups could be cross-linked and the links are broken upon exposure to light thereby forming lower molecular weight materials. In this embodiment, a fluorinated solvent may be selected to selectively remove exposed
15 areas, thereby acting as a positive photopolymer system.

A combination of multiple second monomers or second repeating units having different solubility-altering reactive groups may be used. For example, a fluorinated photopolymer may comprise both acid-forming and an alcohol-forming precursor groups.

20 The copolymer may optionally include additional repeating units having other functional groups or purposes. For example, the copolymer may optionally include a repeating unit that adjusts some photopolymer or film property (e.g., solubility, Tg, light absorption, sensitization efficiency, adhesion, surface wetting, etch resistance, dielectric constant, branching, acid-generation, acid-quenching and the like).

25 Many useful PAG compounds exist that may be added to a photopolymer composition. In the presence of proper exposure and sensitization, this photo-acid

generator will liberate an acid, which will react with the second monomer portion of the fluorinated photopolymer material to transform it into a less soluble form with respect to fluorinated solvents. Although it may be provided as a dispersion, the PAG preferably some solubility in the coating solvent. The amount of PAG required
5 depends upon the particular system, but generally, will be in a range of 0.1 to 6% by weight relative to the copolymer. In an embodiment, the amount of PAG is in a range of 0.1 to 2% by weight relative to the copolymer. In some embodiments, the PAG is fluorinated, non-ionic or both. Some non-limiting useful examples of PAG compounds include 2-[2,2,3,3,4,4,5,5-octafluoro-1-(nonafluorobutylsulfonyloxyimino)-pentyl]-
10 fluorene (ONPF) and 2- [2,2,3,3,4,4,4-heptafluoro-1-(nonafluorobutylsulfonyloxyimino)-butyl]-fluorene (HNBF). Other non-ionic PAGS include: norbornene-based non-ionic PAGs such as *N*-hydroxy-5-norbornene-2,3-dicarboximide perfluorooctanesulfonate, *N*-hydroxy-5-norbornene-2,3-dicarboximide perfluorobutanesulfonate, and *N*-hydroxy-5-norbornene-2,3-dicarboximide
15 trifluoromethanesulfonate; and naphthalene-based non-ionic PAGs such as *N*-hydroxynaphthalimide perfluorooctanesulfonate, *N*-hydroxynaphthalimide perfluorobutanesulfonate and *N*-hydroxynaphthalimide trifluoromethanesulfonate. Suitable PAGs are not limited to those specifically mentioned above and some ionic PAGs can work, too. Combinations of two or more PAGs may be used as well.
20 Methods for preparing polymers from monomers are generally known in the art. In some embodiments, second fluoropolymer materials of the present disclosure may be prepared by dissolving the desired monomers in a reaction solvent such as trifluorotoluene (typically degassed with nitrogen or argon) along with a small amount of a radical initiator such as AIBN or similar material. Typically the reaction mixture is
25 heated, e.g., to above 60 °C for several hours. After cooling to ambient temperature, the copolymer may be precipitated, e.g., in cold methanol, filtered, and then re-dissolved in a target coating solvent, typically a fluorinated solvent such as a hydrofluoroether having a boiling point greater than 90 °C. In some embodiments, the concentration of copolymer for coating may be in a range of 5% to 25% by weight of
30 copolymer solids, depending on target coating thickness, solution viscosity and other factors known in the art.

In some embodiments and unlike the first fluoropolymer material, the second fluoropolymer material may be readily soluble in a second-type of HFE solvent and

have relatively poor solubility in many perfluorinated solvents. In some embodiments, the second fluoropolymer material has good solubility in the same "first-type" of HFE solvents useful for dissolving the first fluoropolymer material. In other embodiments, the second fluoropolymer material has relatively poor or slow solubility first-type HFE
5 solvents.

In an embodiment, the second-type of hydrofluoroether solvent is saturated having fewer than four more perfluorinated carbon atoms than hydrogen-containing atoms. In an embodiment, the second-type hydrofluoroether solvent is a saturated segregated hydrofluoroether having less than five perfluorinated carbon atoms or it is a
10 non-segregated hydrofluoroalkylether. The second-type of HFE solvent typically has a fluorine content of at least 50% by weight, preferably at least 60% by weight, , but typically less than about 69%. Some non-limiting examples of second-type HFE solvents include HFE-7100, HFE-7200, HFE-7600 and HFE-6512.

In an embodiment, the first fluoropolymer layer may be provided by coating a
15 composition including a first fluoropolymer material and a first fluorinated coating solvent that is a perfluorinated solvent or a first-type of HFE or a mixture thereof. In some embodiments, the composition may include other solvents (e.g., second-type of HFE or organic solvents) in lesser amounts relative to the first fluorinated coating solvent In the present embodiment, the second fluoropolymer layer is provided by
20 coating a composition including a second fluoropolymer material, for example a photosensitive fluoropolymer material, and a second fluorinated coating solvent, for example, a second-type of HFE or a first-type HFE. In some embodiments, the composition may include other solvents (e.g., another HFE, a perfluorinated solvent or an organic solvent) in lesser amounts relative to the second fluorinated coating solvent.
25 In an embodiment, in the time frame of coating, the second fluorinated coating solvent does not substantially dissolve the underlying first fluoropolymer layer, thereby forming a discrete coating having only a relatively small or no intermix region between the layers. Although the second fluorinated coating solvent may not substantially dissolve the first fluoropolymer layer, the second fluoropolymer material composition
30 typically wets very well over the first fluoropolymer layer providing a uniform coating.

Processing Agents for embodiments shown in FIGS. 4 and 5.

Referring again to FIG. 5, in certain embodiments, a photosensitive fluoropolymer **132** is used and unexposed regions **132a** are developed (removed) using

a first developing agent. In some embodiments, it has been unexpectedly found that a mixture of fluorinated solvents may be advantageous. In an embodiment the first developing agent may include a mixture of a first fluorinated solvent and a second fluorinated solvent, wherein, when measured in neat first or second fluorinated solvents
5 at about 20 °C, i) the first fluoropolymer layer (e.g., non-patterned fluoropolymer layer **133**) has a higher dissolution rate in the first solvent than in the second solvent, and ii) the second fluoropolymer layer (e.g., unexposed photosensitive fluoropolymer **132, 132a**) has higher dissolution rate in the second solvent than in the first solvent.

In some embodiments, when measured 20 °C, the first fluoropolymer layer has
10 a dissolution rate in the first fluorinated solvent that is at least 2 times higher than in the second fluorinated solvent, alternatively at least 5 times higher, alternatively at least 10 times higher.

In some embodiments, when measured 20 °C, the second fluoropolymer layer has a dissolution rate in the second fluorinated solvent that is at least 2 times higher
15 than in the first fluorinated solvent, alternatively at least 5 times higher, alternatively at least 10 times higher.

In some embodiments, the first fluorinated solvent is a first-type HFE or a perfluorinated solvent. In some embodiments, the first fluorinated solvent is a saturated hydrofluoroether having at least four more perfluorinated carbon atoms than hydrogen-
20 containing carbon atoms. In some embodiments, the first fluorinated solvent is a saturated segregated hydrofluoroether having at least five perfluorinated carbon atoms and less than three hydrogen-containing carbon atoms. In some embodiments, the first fluorinated solvent is a saturated perfluorocarbon, perfluoroalkyl ether or perfluoroalkyl amine. In some embodiments, the first fluorinated solvent is HFE-7300, HFE-7500,
25 HFE-7700, Galden® HT-110, Galden® HT-135, Galden ® HT-170, Fluorinert FC-40, CTSolve-180 or perfluorodecalin. In some embodiments, the first developing agent includes more than one first fluorinated solvent.

In some embodiments, the second fluorinated solvent is a second-type HFE. In some embodiments, the second fluorinated solvent is a saturated hydrofluoroether
30 having fewer than four more perfluorinated carbon atoms than hydrogen-containing atoms and has a fluorine content of at least 60% by weight. In some embodiments, the second fluorinated solvent is a saturated segregated hydrofluoroether having less than five perfluorinated carbon atoms or is a non-segregated hydrofluoroalkylether. In some

embodiments the second fluorinated solvent is HFE-7100, HFE-7200, HFE-7600 or HFE-6512. In some embodiments, the first developing agent includes more than one second fluorinated solvent.

In some embodiments, the first developing agent has a volume ratio of first fluorinated solvent to second fluorinated solvent in a range of about 1:5 to about 5:1, alternatively 1:4 to about 4:1, alternatively 1:3 to about 3:1, alternatively in a range of about 1:2 to about 2:1. In some embodiments, the first developing agent further includes a protic solvent such as an alcohol in a volume range of 0.01 to 10%, alternatively 0.1 to 5%. In some embodiments, the protic solvent is IPA or a fluorine-containing aliphatic alcohol.

In some embodiments, when measured at about 20 °C, a dissolution rate of the first fluoropolymer layer in the first developing agent is about 5 nm/sec or lower. In some embodiments, when measured at 20 °C, a dissolution rate of the second polymer in the first developing agent is about 50 nm/sec or higher.

Under certain conditions, an advantage of the above first developer is that it results in reduced insoluble fluoropolymer and residue, sometimes in the form of very thin layers described as “skin”. Without being bound by theory, it may be that the mixed solvent first developer more fully removes the photosensitive fluoropolymer in the unexposed areas **132a**. It may be that some slight intermixing of layers prevents complete removal of the second fluoropolymer layer material (in this embodiment, a photosensitive fluoropolymer material), which may be trapped in an upper portion of the first fluoropolymer layer that is not easily accessed by the second fluorinated solvent alone. By including the first fluorinated solvent in the first developing agent, trapped photosensitive fluoropolymer material can be solubilized, e.g., through swelling of the first fluoropolymer layer or by some slight dissolution of the first fluoropolymer layer in the first developing agent, or both. If used alone, the second fluorinated solvent may not be able to penetrate the first polymer layer matrix and may be unable to reach trapped photosensitive fluoropolymer material. When the undercut developing agent is applied, the presence of the photosensitive fluoropolymer material in the unexposed portions may result in a barrier to development or result in formation of skin or debris.

Further, the photosensitive fluoropolymer in the supposedly unexposed area **132a**, may have received some small amount of exposure due to light scattering or light

piping causing a small amount of it to have reduced solubility. In this case, adding the protic solvent, in addition to the first fluorinated solvent and second fluorinated solvent, may help solubilize photosensitive fluoropolymer where some of the solubility-altering groups have been switched.

5 In some embodiments, the first developing agent is formulated so that the development of the first fluoropolymer layer is slow. Although it is possible to formulate the system so that a single developing agent readily solubilizes both unexposed photosensitive second fluoropolymer layer and the first fluoropolymer layer, it has unexpectedly been found that the exposed substrate surface may adsorb
10 photosensitive fluoropolymer residue resulting in device problems. By processing sequentially using the above first developing agent and then the undercut developing agent (described below) the exposed substrate surface does not contact any substantial amount of solubilized photosensitive fluoropolymer. The highly fluorinated first fluoropolymer layer material has less tendency to leave a residue than the less
15 fluorinated photosensitive fluoropolymer. Further, it has been found that process and undercut profile can be more carefully controlled by application of the first developing agent tailored to remove the portions of the second fluoropolymer layer, followed by application of the undercut profile developing agent tailored to provide a controlled undercut profile.

20

Undercut developing agent

In embodiments as described in FIGS. 4 and 5, undercut developing agent generally includes a first-type HFE or a perfluorinated solvent or a mixture of both. In some embodiments, the undercut profile developing agent includes HFE-7300, HFE-
25 7500, HFE-7700, Galden® HT-110, Galden® HT-135, Galden ® HT-170, Fluorinert FC-40, CTSolve-180 or perfluorodecalin. In some embodiments, the undercut profile developing agent is a mixture of first-type HFE solvents, alternatively a mixture of perfluorinated solvents. In some embodiments, perfluoroalkyl ethers such as Galden® HT-110, Galden® HT-135 and Galden ® HT-170 are used in a mixture with another
30 perfluorinated solvent or with a first-type HFE. In some embodiments, the undercut developing agent includes the same solvent as the first fluorinated solvent in the first developing agent. In some embodiments, the undercut developing agent includes another solvent in a minor amount, i.e., other than a first-type HFE or a perfluorinated solvent.

In some embodiments, the dissolution rate of the first fluoropolymer layer in the undercut developing agent is in a range of about 6 nm/sec to about 100 nm/sec, alternatively in a range of about 10 nm/sec to about 75 nm/sec, alternatively in a range of about 20 nm/sec to about 60 nm/sec. Target development rates and profile undercut performance may be achieved by adjusting development conditions: time, temperature, and chemical formulation of the undercut profile developing agent. In some embodiments, the undercut developing agent is contacted with the patterned precursor structure in the presence of some first developing agent. That is, in such embodiments, the first developing agent is not first removed or dried, but rather, the undercut developing agent acts to dilute and wash away the first developing agent.

General Process Considerations

Whether forming a fluoropolymer structure having an undercut profile as in embodiments like FIGS. 1 and 2, or as in FIGS 4 or 5, or as in similar embodiments, the developing and rinse agents may optionally be applied in a manner so that there is no drying step until after the rinse, i.e., no drying from the first development step through to the final rinse. In some embodiments, this may reduce unwanted residue or debris from forming on the substrate. Alternatively, in some embodiments, there may be one or more drying steps or partial drying steps, for example, between the undercut development and the rinse, between the first development and the undercut development, or both. In some embodiments, the developing agents may be applied to a stationary substrate for a predetermined time and washed away with one or more subsequent processing agents. In some embodiments, a stationary substrate may be provided in a tank that may be filled with a processing agent, optionally replenished, drained and refilled with a subsequent processing agent. In some embodiments, the substrate may be provided in a horizontal orientation with processing agents provided over top substrate surface (e.g. by spray coating, slot die coating or the like), wherein subsequent processing agents or replenishment causes excess volume simply to spill over the substrate edge. The substrate may be stationary or may move from one processing station to another processing station. In some embodiments, the substrate moves from tank to tank, wherein such tanks may have different processing agents or they may the same general processing agent, but provided in a counter current replenishment format. The particular chemical formulation for the first developing agent, the undercut developing agent or the rinse agent may be changed as a function of

time. For example, the concentration of one solvent component may be increased (or decreased) during a particular process step. Processing solvents may be recycled and reused.

In some embodiments, the various development and rinsing steps may be performed at about the same temperature, such same temperature falling within a range of about 15 °C to about 35 °C, alternatively about 20 °C to about 30 °C. Alternatively, the development and rinsing steps may be performed at different temperatures (e.g., greater than 2 °C difference). As mentioned, in some embodiments, the rinse agent may be applied at a temperature lower than the undercut developing agent. In some embodiments the rinse agent temperature may be lower than 15 °C.

In some embodiments, one or more (or all) patterning steps are done under an inert atmosphere, i.e., an environment having low water or low oxygen, or both. For example, applications of coatings, photo-exposure, development steps, rinsing and drying may all be carried out under inert atmosphere. In some embodiments, the inert atmosphere is primarily dry air, dry nitrogen or dry argon.

## OLED Devices

### OLED Structure

A non-limiting example of an OLED device **10** is shown in FIG. 6 and includes anode **11**, hole-injecting layer (HIL) **12**, hole-transporting layer (HTL) **13**, electron-blocking layer (EBL) **14**, light-emitting layer (LEL) **15** (sometimes referred to in the art as an emissive layer or EML), hole-blocking layer (HBL) **16**, electron-transporting layer (ETL) **17**, electron-injecting layer (EIL) **18** and cathode **19**. The layers between the anode and cathode are often collectively referred to as the organic EL medium **20**. There are many other OLED layer architectures known in the art having fewer or additional layers and there can be overlap in layer functionality. For example, if an EBL is used, it typically also has hole-transporting properties in addition to electron-blocking properties. An HBL, if used, typically has electron-transporting properties. The LEL might have predominantly hole-transporting or electron-transporting properties, or it might have both. There can be multiple light emitting layers. So-called "tandem" architecture is known that includes one or more charge separation layers between light-emitting stacks that can double current efficiency.

Some non-limiting examples of materials useful for OLED devices are discussed below. Although the emphasis is on organic EL medium materials that can be vapor deposited, certain embodiments of the present disclosure may instead use solution deposited OLED materials. A few non-limiting examples of OLED material and structures can be found in US 8106582 and US 7955719, the entire contents of which are incorporated by reference.

When EL emission is viewed through the anode, the anode should be substantially transparent to the emission of interest. The term "transparent" herein means that at least 30% of emitted light is transmitted, preferably at least 50%. Common transparent anode materials used in the present disclosure are indium-tin oxide (ITO), indium-zinc oxide (IZO), and tin oxide, but other metal oxides can work including, but not limited to, aluminum- or indium-doped zinc oxide, magnesium-indium oxide, and nickel-tungsten oxide. In addition to these oxides, metal nitrides such as gallium nitride, and metal selenides such as zinc selenide, and metal sulfides such as zinc sulfide, can be used as the anode. For applications where EL emission is viewed only through the cathode electrode, the transmissive characteristics of the anode are immaterial and many conductive materials can be used, regardless if transparent, opaque, or reflective. Example conductors for the present disclosure include, but are not limited to, gold, iridium, molybdenum, palladium, and platinum. Unless unique HIL materials are used, typical anode materials have a work function of at least 4.0 eV.

If EL emission is viewed through the cathode, it must be transparent or nearly transparent. For such applications, metals must be thin (preferably less than 25 nm) or one may use transparent conductive oxides (e.g. indium-tin oxide, indium-zinc oxide), or a combination of these materials. Some non-limiting examples of optically transparent cathodes have been described in more detail in U.S. Pat. No. 5,776,623. If EL emission is not viewed through the cathode, any conductive material known to be useful in OLED devices may be selected, including metals such as aluminum, molybdenum, gold, iridium, silver, magnesium, the above transparent conductive oxides, or combinations of these. Desirable materials promote electron injection at low voltage and have effective stability. Useful cathode materials often contain a low work function metal ($<4.0$ eV) or metal alloy. Cathode materials can be deposited, for example, by evaporation, sputtering, or chemical vapor deposition.

The HIL can be formed of a single material or a mixture of materials. The hole-injecting layer may be divided into several layers having different composition. The

hole-injecting material can serve to improve the film formation property of subsequent layers and to facilitate injection of holes into the hole-transporting layer. Suitable materials for use in the hole-injecting layer include but are not limited to porphyrin and phthalocyanine compounds as described in U.S. Pat. No. 4,720,432, thiophene-
5 containing compounds, phosphazine compounds, and certain aromatic amine compounds. The HIL may include an inorganic compound such as a metal oxide (e.g., molybdenum oxide), metal nitride, metal carbide, a complex of a metal ion and organic ligands, and a complex of a transition metal ion and organic ligands. Suitable materials for use in the hole-injecting layer may include plasma-deposited fluorocarbon polymers
10 (CFx) as described in U.S. Pat. No. 6,208,075, certain hexaazatriphenylene derivatives as described in U.S. Pat. No. 6,720,573 B2 (e.g. hexacyanohexaazatriphenylene) or tetracyanoquinone derivatives such as F4TCNQ. The hole-injecting layer can also be composed of two components: for example, an aromatic amine compound, doped with a strong oxidizing agent, such as dipyrazino[2,3-f:2′,3′-h]quinoxalinehexacarbonitrile,
15 F4TCNQ, or FeCl3.

The HTL can be formed of a single or a mixture of organic or inorganic materials and may be divided into several layers. The hole-transporting layer most commonly includes a tertiary aryl amine, e.g., a benzidine or a carbazole, but instead (or in addition) may comprise a thiophene, or other electron-rich material. EBL
20 materials (if used) are generally selected from the same group as HTL materials and have an electron conduction band significantly higher in energy (more difficult to reduce) than the overlying LEL thereby creating a barrier to further electron transport.

The LEL commonly includes a host material and a light-emitting dopant. Injected holes and electrons recombine in the LEL. Hosts include HTL materials, ETL
25 materials, a mixture of HTL and ETL materials or ambipolar materials readily capable of transporting holes and electrons. Examples of common hosts for singlet emission include polycyclic aromatic compounds such as anthracene derivatives. Examples of common hosts for triplet emission include carbazole compounds and aromatic amines. A wide variety of light-emitting dopants are known and are used to provide the desired
30 emission wavelength by harvesting excitons created from the electron/hole charge injection. Many common singlet emitting dopants are aromatic organic compounds whereas many common triplet emitting dopants are metal complexes of iridium or platinum.

The ETL can be formed of a single or a mixture of organic or inorganic materials and may be divided into several layers. Common ETL materials include metal oxine chelates such as Alq, phenanthroline derivatives such as BCP, triazenes, benzimidazoles, triazoles, oxadiazoles, silane compounds such as silacyclopentadiene
5 derivatives, and borane derivatives. HBL materials (if used) are generally selected from the same group as ETL materials and have hole conduction band significantly lower in energy (more difficult to oxidize) than the underlying LEL thereby creating a barrier to further hole transport.

The EIL may include an ETL material plus a reducing dopant at or near the
10 interface between the cathode and ETL. The reducing dopant can be organic, inorganic, or metal complexes. Common reducing dopants include alkali metals such as Cs or combinations of alkali metals. The EIL may include an alkali or alkaline metal complex, salt or oxide (e.g., lithium quinolate, LiF, CaO) that forms a reducing dopant upon deposition of a cathode material such as aluminum.

15 OLED Deposition

There are many ways to deposit organic EL medium materials onto a substrate including, but not limited to, solution coating, vapor deposition, and transfer from a donor sheet. In certain embodiments of the present disclosure at least some of the organic OLED layers be deposited by vapor deposition means, e.g., physical vapor
20 deposition in a reduced pressure environment. In some embodiments, most or all of the organic EL medium layers are provided by vapor deposition.

Many types of vapor deposition equipment are suitable. Such equipment may use point sources, linear sources, vapor-injection sources, carrier gas-assisted sources (OVPD) and the like. In some embodiments, the vapor plume is preferably highly
25 directional to achieve a controlled line-of-site deposition through a patterned photoresist structure as will be shown later.

OLED Devices/Backplanes

There is no particular limitation on the type of OLED device that may be fabricated based on methods of the present disclosure, so long as some patterning is
30 intended. The present methods are especially directed to full color OLED displays such as active matrix OLED (AMOLED) and passive matrix OLED (PMOLED), but the methods may be used to prepare OLED lighting and signage. OLED device substrates may be rigid or flexible. Support materials include, but are not limited to, glass, polymers, ceramics and metals, and composites or laminates thereof.

AMOLED backplanes typically include an array of independently addressable first (bottom) electrodes that are connected to thin film transistor (TFT) circuitry provided over a substrate typically in a multilayer structure. The TFT may be based on Si, metal oxide or organic semiconductors (OTFT). In addition to the semiconductors, dielectrics and conductors are used to prepare structures that form the transistors, capacitors, wiring…etc. as is known in the art.

OLED Patterning

FIG. 7A is a plan view and FIG. 7B is a sectional view along cut line C-C showing an embodiment of a portion of an OLED substrate **200** or backplane having a support **201** (e.g., flexible or non-flexible glass, plastic or ceramic), a TFT layer portion **202** (which may include multiple layers of wiring, dielectric and semiconductor materials), an array of first bottom electrodes **210**, an array of second bottom electrodes **220**, an array of third bottom electrodes **230** and a pixel-defining layer (PDL) **203**. The pixels are all independently addressable. When the device is complete, the first array of bottom electrodes forms a portion of a first array of independently addressable first OLED devices, the second array of bottom electrodes forms a portion of a second array of independently addressable second OLED devices, the third array of bottom electrodes forms a portion a third array of independently addressable third OLED devices. For example, the first OLED devices may be red-emitting OLED devices (red pixels), the second OLED devices may be green-emitting OLED devices (green pixels), and the third OLED devices may be blue-emitting OLED devices (blue pixels). As shown in FIG. 7A, the arrays are provided in a so-called stripe pattern wherein the pixels are provided in columns of red, green or blue-emitting pixels. Not shown, the stripe pattern may have instead been provided in rows. In other embodiments, the pixels may be provided in an alternative pattern, including but not limited to, pentile patterns which are well known to the skilled artisan. Not shown, the substrate may further include common organic EL medium layers that will make up a portion of each organic EL element. For example, the substrate may include a common HIL and HTL.

FIG. 8 includes sectional views to briefly illustrate how an OLED device may be patterned over OLED substrate from FIG. 7. In FIG. 8A, a fluoropolymer resist structure **221** having an undercut profile may be formed over OLED substrate **200** described in FIG. 7 (for clarity, part numbers for substrate **200** have been omitted in FIG. 8). For example, the fluoropolymer structure may be formed in a manner previously described with respect to FIGS. 4 and 5 and includes a first patterned

fluoropolymer **223** and a patterned layer **222**. In FIG. 8A, the fluoropolymer resist structure has opening(s) **225** in registration with first bottom electrodes **210**.

Referring to FIG. 8B first organic EL medium layer(s) are deposited over the structure of FIG. 8A. A portion of the first organic EL medium layers **217'** is deposited over the fluoropolymer resist structure **211** (specifically, over patterned layer **222**) whereas another portion of the first organic EL medium layers **217** goes through the opening **225** and deposits on the first array of bottom electrodes **210**. In an embodiment, first organic EL medium layers **217** may be intended to emit red light. Although not shown in this embodiment, a first top electrode may be optionally deposited over the organic EL medium layers.

The fluoropolymer resist structure **211** is then removed along with the overlying first organic EL medium layers **217'**. In some embodiments, removal may be done by peeling off the fluoropolymer resist structure, or at least the patterned layer portion of it, along with the overlaying organic EL medium layers. In some embodiments, such peeling off may include the use of an adhesive tape. In some embodiments, removal is achieved by contact with a lift-off agent that dissolves the first patterned fluoropolymer **223** but not patterned layer **222** nor organic EL medium materials (i.e., an orthogonal lift-off agent). This detaches patterned layer **222** and overlying EL medium layers **217'** which are carried away by fluid flow or simple floatation, thereby forming a first intermediate structure **250** as shown in FIG. 8C having a first array of organic EL medium layers **217** provided over bottom electrodes **210**. Alternatively, rather than dissolving the first material layer, the lift-off solvent may swell the lift-off structure thereby causing its delamination or otherwise affect the adhesion between the substrate and the lift-off structure.

The steps described above may be repeated to pattern-deposit second organic EL medium layers **227** (e.g., for emitting green light) over second bottom electrodes **220** and third organic EL medium layers **237** (e.g., for emitting blue light) over third bottom electrodes **230**. A common top electrode **240** may be deposited thereby forming a patterned, full color, active matrix OLED device **260**.

Lift-off Agent

In some embodiments when the fluoropolymer resist structure having an undercut profile includes a first patterned fluoropolymer as in FIGS. 4, 5 or 8, the lift-off agent may include as a primary component a perfluorinated solvent or a first-type of

HFE. In some embodiments, the lift-off agent may include a mixture of such solvents. In some embodiments, the lift-off agent may include an additional solvent in a minor amount that is not a perfluorinated solvent or a first-type HFE. In some embodiments when the fluoropolymer structure having an undercut profile includes a patterned 5 fluoropolymer, such as a patterned photosensitive fluoropolymer, as described in FIGS. 1 – 3, the lift-off agent may include a second-type HFE or a first-type HFE. In some embodiments, the lift-off agent may include a mixture of such solvents. In some embodiments, the lift-off agent may include an additional solvent in a minor amount that is not a second-type HFE or a first-type HFE.

10 In an embodiment, the density of the lift-off agent is greater than the average density of the patterned layer (**122**, **222**), or alternatively greater than the average density of upper portion **118U**. The lift-off agent may optionally be heated to speed the lift-off step so long as such heating is compatible with the device structure and materials. In an embodiment, the dissolution rate of patterned fluoropolymer **123, 223** 15 or lower portion **118L** in the lift-off agent (optionally heated) is at least 20 nm/sec, alternatively at least 50 nm/sec, alternatively at least 75 nm/sec, alternatively at least 100 nm/sec, alternatively at least 150 nm/sec. In an embodiment, the dissolution rate of the lift-off agent (optionally heated) is at least 2 times higher than the dissolution rate in the undercut developing agent, alternatively at least 5 times higher, alternatively at least 20 10 times higher.

In some embodiments, after lift-off, the patterned device is rinsed with additional lift-off solvent or some other lift-off rinse agent. In some embodiments, the lift-off rinse agent includes a perfluoroalkane solvent, a perfluoroalkyl ether solvent, a perfluoroalkyl amine solvent or a first type HFE solvent.

25 Referring again to FIGS. 7 and 8, PDL **203** in conventional OLED devices is typically formed from a polyimide or alternatively silicon oxide. In some embodiments of the present disclosure, it has been unexpectedly found that using a fluorinated PDL material may improve the yield of processes relating to the fluorinated resist structure. In some embodiments, the fluorinated PDL is formed from a photosensitive 30 fluoropolymer as described above. In some embodiments, the photosensitive fluoropolymer is not a cross-linking type of photopolymer. In some embodiments, the photosensitive fluoropolymer used to form the PDL includes an alcohol-forming precursor group. In some embodiments, the photosensitive fluoropolymer used to form the PDL includes an acid-forming precursor group, e.g., a carboxylic acid forming

precursor group. In an embodiment, the photosensitive fluoropolymer used to form the PDL is substantially the same as a photosensitive fluoropolymer used to form the fluorinated resist structure. By “substantially the same” it is meant that the two photosensitive fluoropolymers may include the same switching groups, e.g., a
5 carboxylic acid forming precursor, and the same fluorine-containing groups, although potentially in different amounts. In some embodiments the fluorinated PDL has a total fluorine content of at least at least 15%. In an embodiment, the total fluorine content is in a range of 15% to 60%, alternatively 30 to 60%, or alternatively 35 to 55%. In some embodiments, the sidewall angle of the fluorinated PDL is 45° or lower, i.e., the angle
10 of the PDL with the bottom electrodes. In some embodiments, the PDL has a thickness in a range of about 0.1 μm to about 2.0 μm, alternatively about 0.2 μm to about 1.5 μm, alternatively about 0.3 μm to about 1.0 μm.

In an embodiment, the fluorinated PDL may be provided by coating a photosensitive fluoropolymer over a substrate, e.g., an OLED substrate, exposing the
15 coating to patterned radiation, and developing in a fluorinated solvent, e.g., a PDL developing agent including a hydrofluoroether solvent in a manner described previously. In an embodiment, after development, the fluorinated PDL is baked (in an oven, on a hot plate, by IR radiation or other means) at a temperature of at least 100 °C, alternatively, at least 150 °C, alternatively, at least 180 °C. In an embodiment, after
20 development, the fluorinated PDL is baked at a temperature in a range of about 100 °C up to about 200 °C, alternatively in a range of about 150 °C up to about 190 °C. In an embodiment, the baking time may be in a range of about 30 seconds up to about 30 minutes, alternatively, in a range of about 1 minute to about 20 minutes, alternatively in a range of about 3 minutes to about 15 minutes. In an embodiment, after development
25 or after baking, the PDL may be subjected to a plasma etch, for example an oxygen plasma etch.

It has been observed that fluoropolymer resist structures may adhere better to a substrate having a fluorinated PDL, for example, a fluorinated PDL having carboxylic acid groups. Fluorinated PDL made using the methods and materials described above
30 may also have the advantage of lower outgassing of water vapor (unlike polyimides) and lower overall processing temperatures, thereby improving compatibility with underlying layers that may be temperature sensitive.

In some embodiments, referring again to FIG. 8A and to plan view FIG. 9, openings **225** may be patterned in the form of holes over each of the first electrodes.

One of the openings **225** is highlighted as a dotted outline in FIG. 9. In some embodiments, for example when the pixels are provided in a stripe pattern, openings **225** may be provided in the form of long open channels (plan view FIG. 10). During undercut development or rinse steps, relative to a pattern of holes, the channel structure
5 may in some embodiments allow improved solution mixing and/or contact in or near the patterned areas. This may reduce residue, improve uniformity, improve yield, make process more robust to changes, or a combination of such advantages.

Embodiments

10 Some non-limiting embodiments of the present disclosure are described below

Embodiment Set A

1. A method of forming a fluoropolymer resist structure having an undercut profile comprising:

over a device substrate, forming a patterned precursor structure comprising a
15 fluoropolymer layer, the patterned precursor structure having a pattern of first and second surface regions;

contacting the patterned precursor structure with an undercut developing agent comprising a hydrofluoroether solvent, a perfluorinated solvent or both, wherein the undercut developing agent removes a portion of the fluoropolymer layer in registration
20 with the first surface region, thereby forming a first patterned fluoropolymer structure having a first undercut profile; and

contacting the first patterned fluoropolymer structure with a rinse agent comprising a fluorinated rinse solvent, wherein

the fluoropolymer layer has a dissolution rate in the undercut developing agent
25 that is at least 3 times greater than a dissolution rate in the rinse agent.

2. The method of embodiment 1 wherein the second surface region includes a patterned layer provided over the fluoropolymer layer, wherein the patterned layer is substantially insoluble in the undercut developing agent and the rinse agent.

3. The method of embodiment 2 wherein the patterned layer is provided by
30 printing.

4. The method of embodiment 2 wherein the patterned layer is formed from a photopolymer.

5. The method of embodiment 4 wherein the photopolymer is a photosensitive fluoropolymer.

6. The method according to any of embodiments 1 – 5, wherein the fluoropolymer layer comprises a perfluorinated polymer.

7. The method according to any of embodiments 1 – 6, wherein the fluoropolymer layer comprises a fluoropolymer having perfluorinated cyclic ether or dioxol groups.

8. The method according to any of embodiments 1 – 7, wherein the fluoropolymer layer comprises an amorphous fluoropolymer.

9 The method of embodiment 1, wherein the fluoropolymer layer is a photosensitive fluoropolymer layer having a lower portion proximate the substrate and an upper portion distal the substrate, and the patterned precursor structure is formed by exposing the photosensitive fluoropolymer to patterned radiation to form unexposed and exposed areas in accordance with the patterned areas, wherein the unexposed areas correspond to the first surface region and the exposed areas correspond to the second surface region.

10. The method of embodiment 9, wherein the lower portion of the exposed area of the photosensitive fluoropolymer has a dissolution rate in the undercut developing agent that is at least 5 times higher than the dissolution rate for the upper portion.

11. The method according to any of embodiments 1 – 10, wherein the fluoropolymer layer has a dissolution rate in the undercut developing agent that is at least 5 times greater than a dissolution rate in the rinse agent.

12. The method according to any of embodiments 1 – 9 wherein the fluoropolymer layer has a dissolution rate in the undercut developing agent that is at least 10 times greater than a dissolution rate in the rinse agent.

13. The method according to any of embodiments 1 – 12 wherein the fluoropolymer layer has a dissolution rate in the rinse agent that is less than 5 nm/sec.

14. The method according to any of embodiments 1 – 13 wherein the fluoropolymer layer has a dissolution rate in the rinse agent that is less than 2 nm/sec.

15. The method according to any of embodiments 1 – 14 wherein the fluorinated rinse solvent is a perfluoroalkyl ether.

16. The method according to any of embodiments 1 – 15 wherein the fluorinated rinse solvent is a perfluoroalkane.

17. The method according to any of embodiments 1 – 16 wherein the fluorinated rinse solvent is a perfluoroalkyl amine.

18. The method according to any of embodiments 1 – 17, wherein the fluorinated rinse solvent is a hydrofluoroether.

19. The method according to any of embodiments 1 – 18 wherein the rinse agent has a boiling point of about 135 °C or lower.

5 20. The method according to any of embodiments 1 – 18 wherein the rinse agent has a boiling point of about 110 °C or lower.

21. The method according to any of embodiments 1 – 18 wherein the rinse agent has a boiling point of about 100 °C or lower.

22. The method according to any of embodiments 1 – 18, wherein the rinse
10 agent has a boiling point of about 80 °C or lower.

23. The method according to any of embodiments 1 - 18, wherein the rinse agent has a boiling point of about 70 °C or lower.

24. The method according to any of embodiments 1 – 23 wherein the rinse agent has a kinematic viscosity lower than a kinematic viscosity of the undercut
15 developing agent.

25. The method according to any of embodiments 1 – 24 wherein the rinse agent has a kinematic viscosity of 2.0 centistokes or less.

26. The method according to any of embodiments 1 – 24 wherein the rinse agent has a kinematic viscosity of about 1.8 centistokes or less,

20 27. The method according to any of embodiments 1 – 24 wherein the rinse agent has a kinematic viscosity of about 1.5 centistokes or less.

28. The method according to any of embodiments 1 – 27 wherein there is no drying step between application of the undercut developing agent and the rinse agent.

29. The method according to any of embodiments 1 – 28, wherein the
25 contacting the first fluoropolymer structure with the rinse agent is conducted for a period of time of 30 seconds or less.

30. The method according to any of embodiments 1 – 28, wherein the contacting the first fluoropolymer structure with the rinse agent is conducted for a period of time of 15 seconds or less.

30 31. The method according to any of embodiments 1 – 30, wherein the contacting the first fluoropolymer structure with the rinse agent is conducted for a period of time and includes an initial contact with the rinse agent having a first rinse

composition and a later contact during the period of time with the rinse agent having a second rinse composition different from the first rinse composition.

32. The method according to embodiment 31 wherein the second rinse composition has lower boiling point than the first rinse composition.

5 33. The method of embodiment 31 or 32, wherein the fluoropolymer layer has a dissolution rate in the second rinse composition that is at least 3 times lower than a dissolution rate in the first rinse composition.

34. The method according to any of embodiments 1 – 33, wherein the undercut developing agent is provided at a first temperature and the rinse agent is

10 provided at a second temperature, and wherein the second temperature is at least 5 °C lower than the first temperature.

35. The method according to embodiment 34, wherein the second temperature is at least 10 °C lower than the first temperature.

36. A method of patterning a device using the fluoropolymer resist structure

15 made according to any of embodiments 1 – 35, wherein the fluoropolymer resist structure is used as a lift-off structure.

37. The method of embodiment 36 wherein the device is an OLED, an OTFT or an organic electronic sensor.

38. The method of claim 37, wherein the device is an active matrix OLED

20 display having an array of red pixels, an array of green pixels, and an array of blue pixels.

39. The method of claim 38, wherein one or more of the arrays of red, green, and blue pixels are provided in a stripe pattern.

40. The method according to any of embodiments 36 – 39, wherein the

25 device comprises a pixel definition layer, the pixel definition layer including a fluoropolymer having carboxylic acid groups and a fluorine content of at least 15% by weight.

Embodiment Set B

1B. A method of forming a fluoropolymer resist structure having an

30 undercut profile comprising:

coating a first fluoropolymer layer over a substrate;

coating a photosensitive second fluoropolymer layer over the first fluoropolymer layer;

exposing the photosensitive second fluoropolymer layer to patterned radiation to form an exposed structure, wherein the photosensitive second fluoropolymer layer of the exposed structure includes exposed and unexposed portions; and

forming a patterned precursor structure by applying a first developing agent to the exposed structure to form a patterned second fluoropolymer layer, the first developing agent comprising a mixture of a first fluorinated solvent and a second fluorinated solvent,

wherein, when measured in neat first and second fluorinated solvents at 20 °C,

i) the first fluoropolymer layer has a higher dissolution rate in the first fluorinated solvent than in the second fluorinated solvent, and

ii) the unexposed portion of the second fluoropolymer layer has higher dissolution rate in the second fluorinated solvent than in the first fluorinated solvent.

2B. The method of embodiment 1B wherein the first developing agent has a volume ratio of first fluorinated solvent to second fluorinated solvent in a range of about 1:5 to about 5:1, alternatively 1:4 to about 4:1, alternatively 1:3 to about 3:1, alternatively in a range of about 1:2 to about 2:1.

3B. The method according to embodiment 1B or 2B wherein a dissolution rate of the first fluoropolymer layer in the first developing agent is 5 nm/sec or lower.

4B. The method according to any of embodiments 1B – 3B wherein a dissolution rate of the unexposed portions of the photosensitive second fluoropolymer layer in the first developing agent is 50 nm/sec or higher.

5B. The method according to any of embodiments 1B – 4B wherein the first fluorinated solvent is a first hydrofluoroether.

6B. The method of embodiment 5B wherein the first hydrofluoroether solvent is a saturated hydrofluoroether having at least four more perfluorinated carbon atoms than hydrogen-containing carbon atoms.

7B. The method of embodiment 5B or 6B wherein the first hydrofluoroether solvent is a saturated segregated hydrofluoroether having at least five perfluorinated carbon atoms and less than three hydrogen-containing carbon atoms.

8B. The method according to any of embodiments 1B – 4B wherein the first fluorinated solvent is a first perfluorinated solvent.

9B. The method according to embodiment 8B wherein the first perfluorinated solvent is a saturated perfluoroalkane, perfluoroalkyl ether or perfluoroalkyl amine.

10B. The method according to any of embodiments 1B – 9B where in the second fluorinated solvent is a second hydrofluoroether.

11B. The method according to embodiment 10B wherein the second hydrofluoroether solvent is a saturated hydrofluoroether having fewer than four more perfluorinated carbon atoms than hydrogen-containing atoms and has a fluorine content of at least 60% by weight.

12B. The method according to embodiment 10B or 11B wherein the second hydrofluoroether solvent is a saturated segregated hydrofluoroether having less than five perfluorinated carbon atoms or is a non-segregated hydrofluoroalkylether.

13B. The method according to any of embodiments 1B – 12B further comprising applying an undercut developing agent to solubilize a portion of the first fluoropolymer layer to form a first patterned fluoropolymer structure having a first undercut profile, the undercut developing agent comprising a third hydrofluoroether solvent or a second perfluorinated solvent or a mixture thereof, and may optionally further comprise a fourth hydrofluoroether solvent or a third perfluorinated solvent.

14B. The method of embodiment 13B wherein the third or fourth hydrofluoroether solvent is a saturated hydrofluoroether having at least four more perfluorinated carbon atoms than hydrogen-containing carbon atoms.

15B. The method according to embodiment 13B or 14B wherein the third or fourth hydrofluoroether solvent is a saturated segregated hydrofluoroether having at least five perfluorinated carbon atoms and less than three hydrogen-containing carbon atoms.

16B. The method according to any of embodiments 13B – 15B wherein the third or fourth hydrofluoroether solvent is the same as the first hydrofluoroether solvent of the first developing agent.

17B. The method according to any of embodiments 13B – 16B wherein the second or third perfluorinated solvent is a perfluoroalkane, perfluoroalkyl ether or perfluoroalkyl amine.

18B. The method according to any of embodiments 1B – 17B wherein the first fluoropolymer layer has a higher weight percent of fluorine than the photosensitive second fluoropolymer layer.

19B. The method according to any of embodiments 1B – 18B wherein the first fluoropolymer layer has a fluorine content of at least 50% by weight.

20B. The method according to any of embodiments 1B – 19B wherein the photosensitive second fluoropolymer layer has a fluorine content in a range of about 15% to about 60% by weight.

21B. The method according to any of embodiments 1B – 20B wherein the first fluoropolymer layer comprises a perfluorinated polymer.

22B. The method according to any of embodiments 21B wherein the perfluorinated polymer includes perfluorinated cyclic ether or dioxol groups.

23B. The method according to embodiment 21B or 22B wherein the perfluorinated polymer is amorphous.

24B. The method according to any of embodiments 13B – 23B further comprising applying a rinse agent to the first patterned fluoropolymer structure, wherein the rinse agent comprises a fluorinated solvent.

25B. The method of embodiment 24B wherein the fluoropolymer layer has a dissolution rate in the undercut developing agent that is at least 3 times greater than a dissolution rate in the rinse agent.

26B. The method according to any of embodiments 13B – 25B wherein there is no drying step between application of the first developing agent and the undercut developing agent.

27B. A method of patterning a device using the fluoropolymer resist structure made according to any of embodiments 1B – 26B, wherein the fluoropolymer resist structure is used as a lift-off structure.

28B. The method of embodiment 27B wherein the device is an OLED, an OTFT or an organic electronic sensor.

29B. The method of embodiment 28B, wherein the device is an active matrix OLED display having an array of red pixels, an array of green pixels, and an array of blue pixels.

30B. The method of embodiment 29B, wherein one or more of the arrays of red, green, and blue pixels are provided in a stripe pattern.

31B. The method according to any of embodiments 27B – 30B, wherein the device comprises a pixel definition layer, the pixel definition layer including a fluoropolymer having carboxylic acid groups and a fluorine content of at least 15% by weight.

Embodiment Set C

1C. An organic electronic device comprising a pixel definition layer, the pixel definition layer including a fluoropolymer having carboxylic acid groups.

2C. The device of embodiment 1C wherein the device is an active matrix
5 OLED.

3C. The device of embodiment 1C or 2C wherein the fluoropolymer having carboxylic acid groups has a fluorine content of at least 15% by weight.

4C. The device according to any of embodiments 1C – 3C wherein the fluoropolymer having carboxylic acid groups has a fluorine content in a range of about
10 15% to about 60% by weight, alternatively, about 30% to about 60% by weight.

5C. The device according to any of embodiments 1C – 4C wherein the pixel definition layer has a thickness in a range of about 0.2 μm to about 1.5 μm.

15

We Claim:

1. A method of forming a fluoropolymer resist structure having an undercut profile comprising:

5 over a device substrate, forming a patterned precursor structure comprising a fluoropolymer layer, the patterned precursor structure having a pattern of first and second surface regions;

contacting the patterned precursor structure with an undercut developing agent comprising a hydrofluoroether solvent, a perfluorinated solvent or both, wherein the

10 undercut developing agent removes a portion of the fluoropolymer layer in registration with the first surface region, thereby forming a first patterned fluoropolymer structure having a first undercut profile; and

contacting the first patterned fluoropolymer structure with a rinse agent comprising a fluorinated rinse solvent, wherein

15 the fluoropolymer layer has a dissolution rate in the undercut developing agent that is at least 3 times greater than a dissolution rate in the rinse agent.

2. The method of claim 1, wherein the second surface region includes a patterned layer provided over the fluoropolymer layer, wherein the patterned layer is

20 substantially insoluble in the undercut developing agent and the rinse agent.

3. The method of claim 2, wherein the patterned layer is formed from a photosensitive fluoropolymer.

25 4. The method of claim 1, wherein the fluoropolymer layer comprises a perfluorinated polymer having cyclic ether or dioxol groups.

5. The method of claim 1, wherein the fluoropolymer layer has a dissolution rate in the undercut developing agent that is at least 10 times greater than

30 the dissolution rate in the rinse agent.

6. The method of claim 1, wherein the fluoropolymer layer has a dissolution rate in the rinse agent that is less than 5 nm/sec.

7. The method of claim 1, wherein the fluorinated rinse solvent is a perfluoroalkyl ether.

8. The method of claim 1, wherein the fluorinated rinse solvent is a
5 hydrofluoroether.

9. The method of claim 1, wherein the rinse agent has a boiling point lower than the boiling point of the undercut developing agent.

10 10. The method of claim 1, wherein the rinse agent has a boiling point of 135 °C or lower.

11. The method of claim 1, wherein the rinse agent has a kinematic viscosity lower than the kinematic viscosity of the undercut developing agent.
15

12. The method of claim 1, wherein the rinse agent has a kinematic viscosity of 1.8 centistokes or less,

13. The method of claim 1, wherein there is no drying step between
20 contacting with the undercut developing agent and contacting with the rinse agent.

14. The method of claim 1, wherein the contacting the first fluoropolymer structure with the rinse agent is conducted for a period of time and includes an initial contact with the rinse agent having a first rinse composition and a later contact during
25 the period of time with the rinse agent having a second rinse composition different from the first rinse composition.

15. The method of claim 14, wherein:

30 i) the second rinse composition has lower boiling point than the first rinse composition;

ii) the fluoropolymer layer has a dissolution rate in the second rinse composition that is at least 3 times lower than a dissolution rate in the first rinse composition; or

5 iii) both i) and ii).

16. The method of claim 1, wherein the undercut developing agent is provided at a first temperature and the rinse agent is provided at a second temperature, and wherein the second temperature is at least 5 °C lower than the first temperature.

10

17. A method of patterning a device using the fluoropolymer resist structure made according to claim 1, wherein the fluoropolymer resist structure is used as a lift-off structure, and wherein the device is an OLED, an OTFT or an organic electronic sensor.

15

18. The method of claim 17, wherein the device is an active matrix OLED display having an array of red pixels, an array of green pixels, and an array of blue pixels.

20 19 The method of claim 18, wherein one or more of the arrays of red, green, and blue pixels are provided in a stripe pattern.

20. The method of claim 18, wherein the active matrix OLED display comprises a pixel definition layer, the pixel definition layer including a fluoropolymer
25 having carboxylic acid groups and a fluorine content of at least 15% by weight.

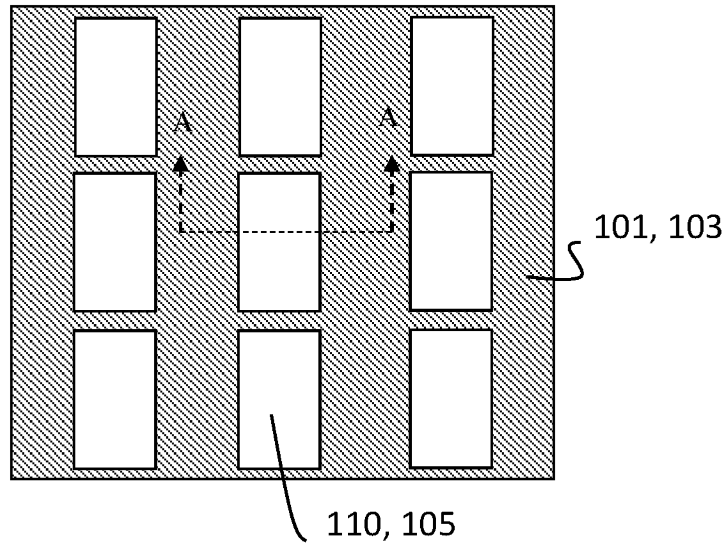



FIG. 1A

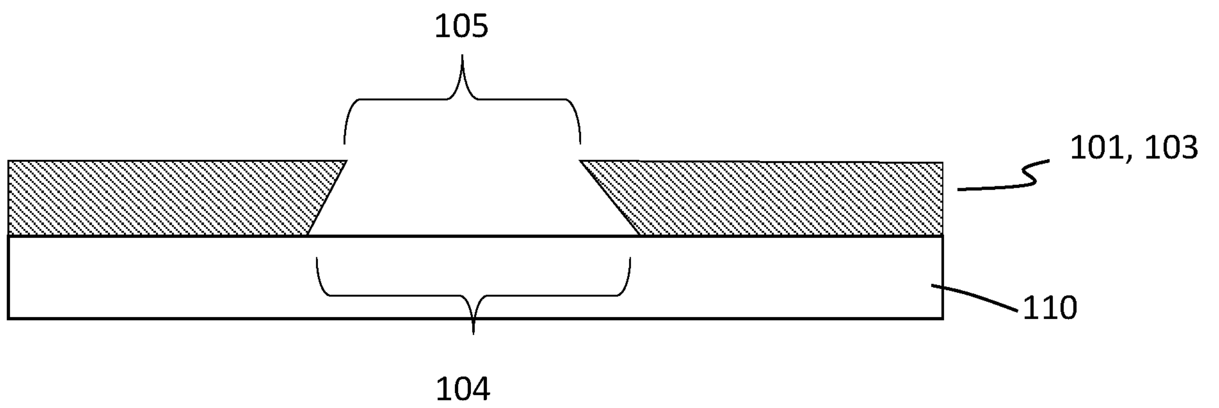



FIG. 1B

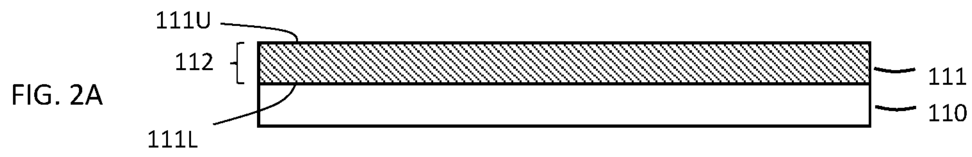



FIG. 2A

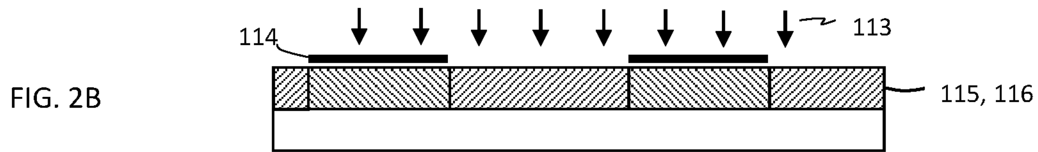



FIG. 2B

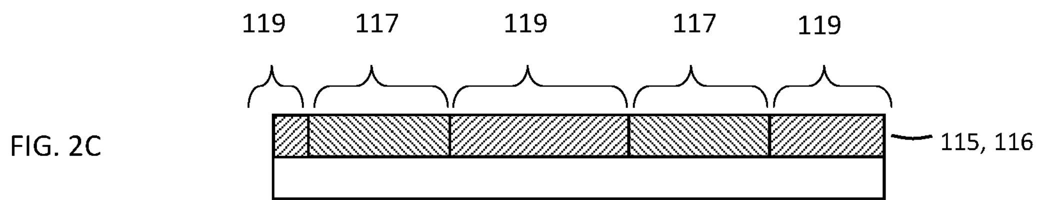



FIG. 2C

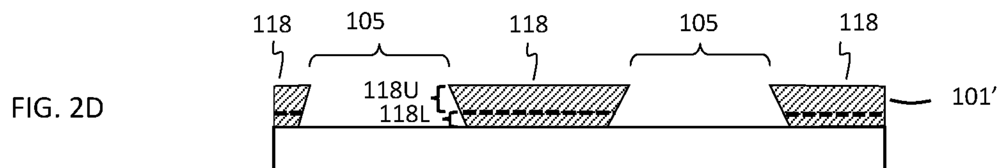



FIG. 2D

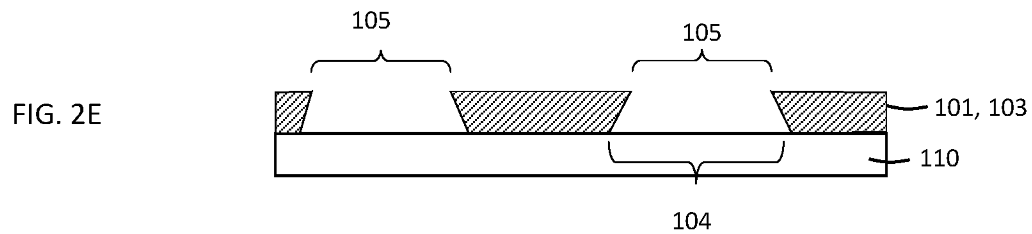



FIG. 2E

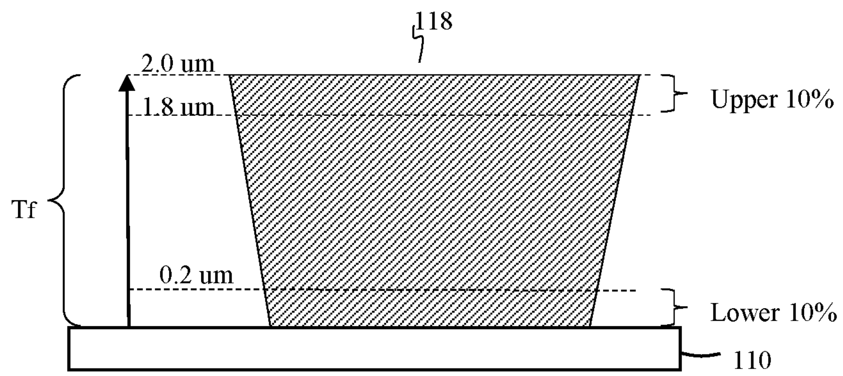



FIG. 3

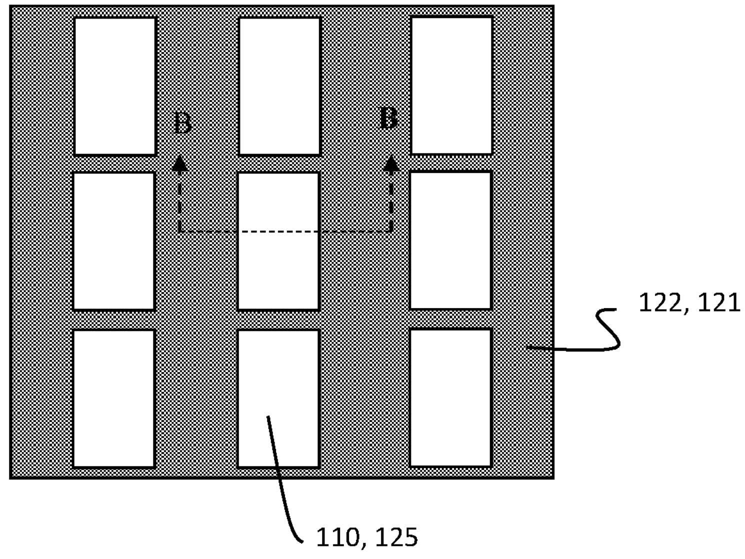



FIG. 4A

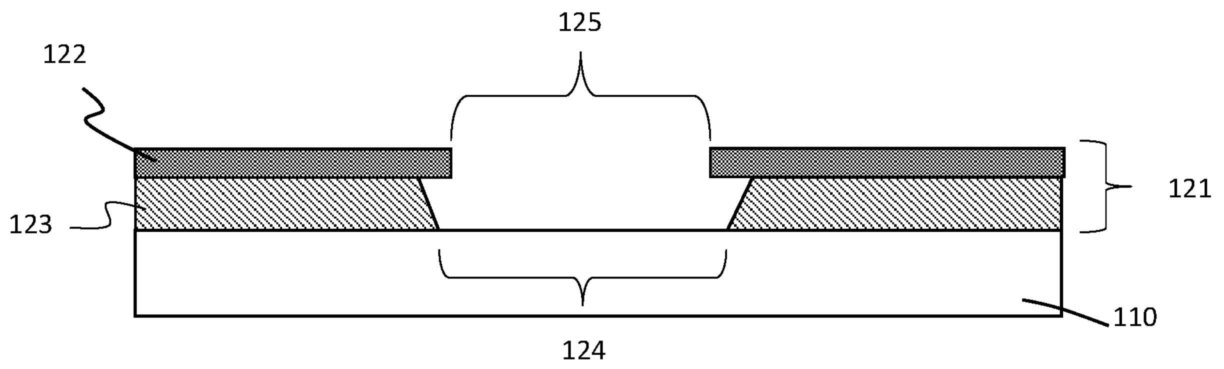



FIG. 4B

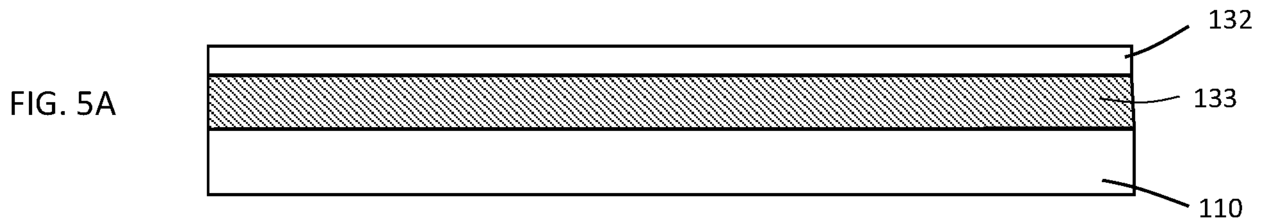



FIG. 5A

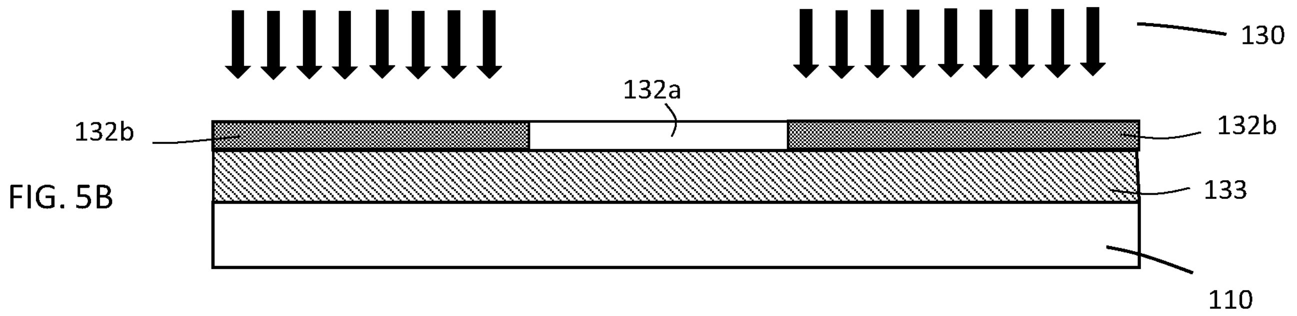



FIG. 5B

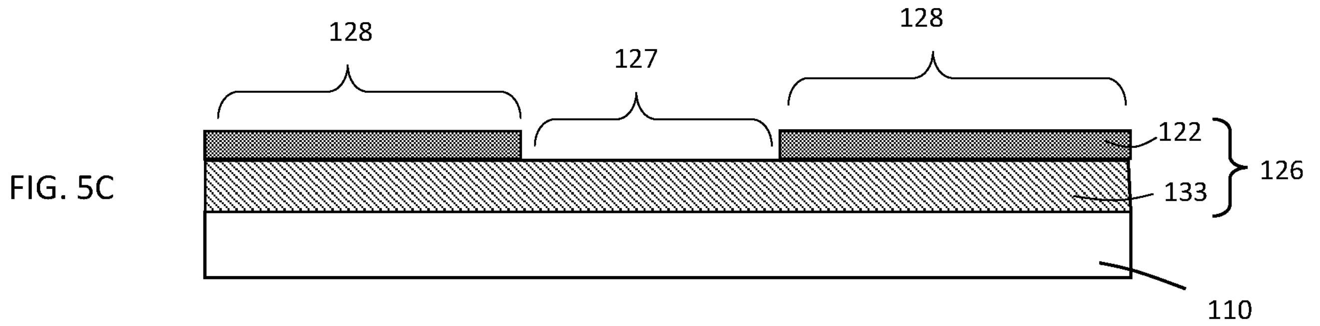



FIG. 5C

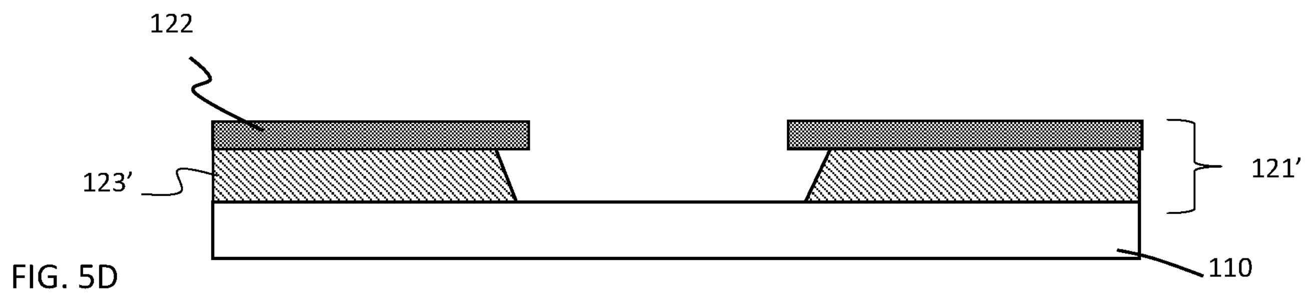



FIG. 5D

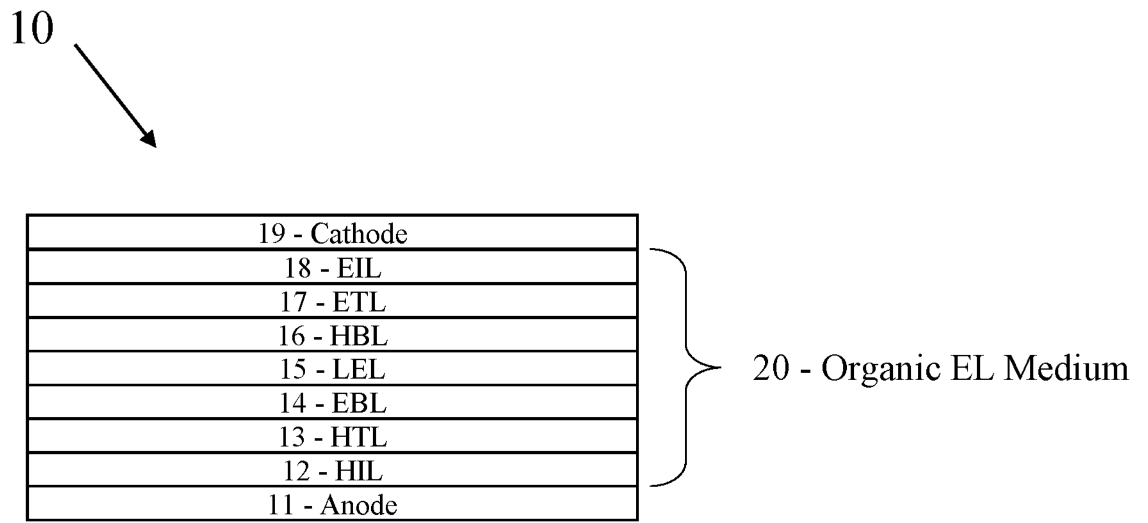



FIG. 6

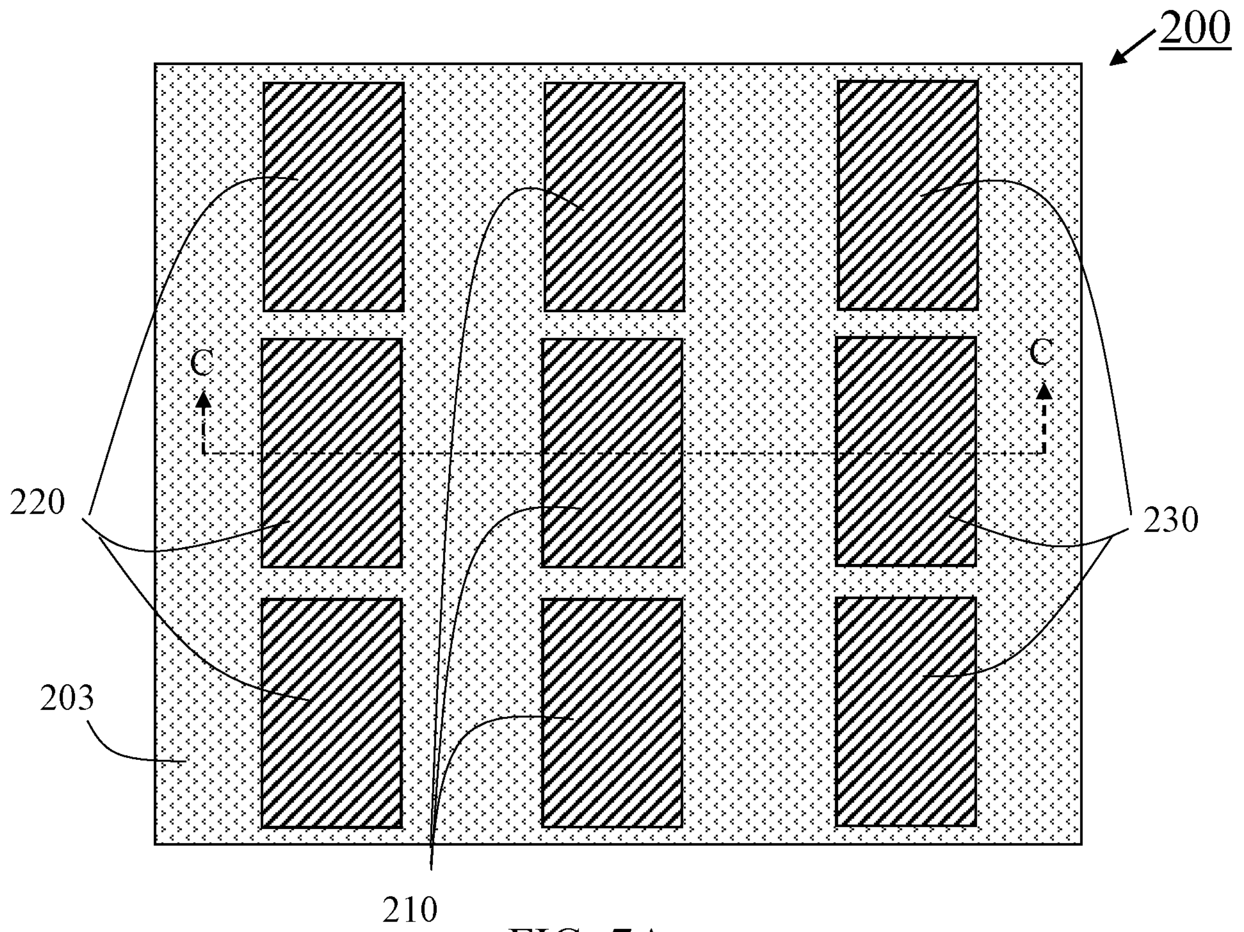



FIG. 7A

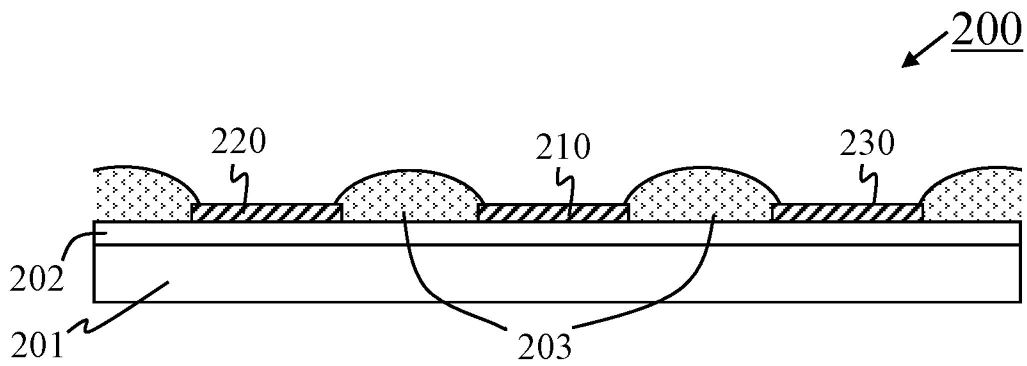



FIG. 7B

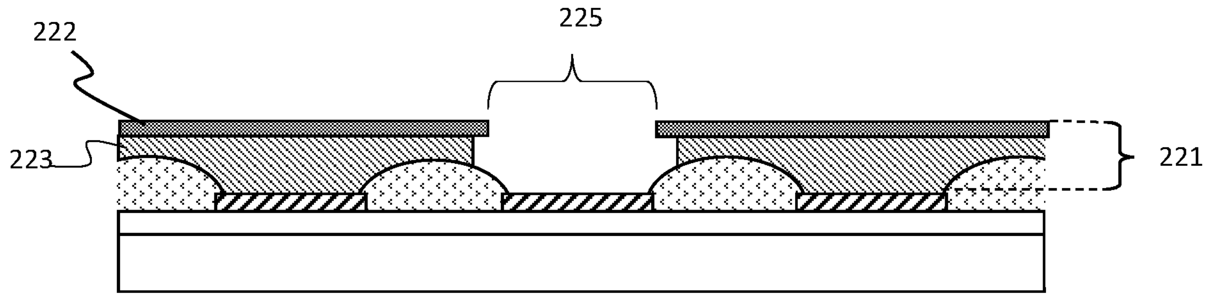



FIG. 8A

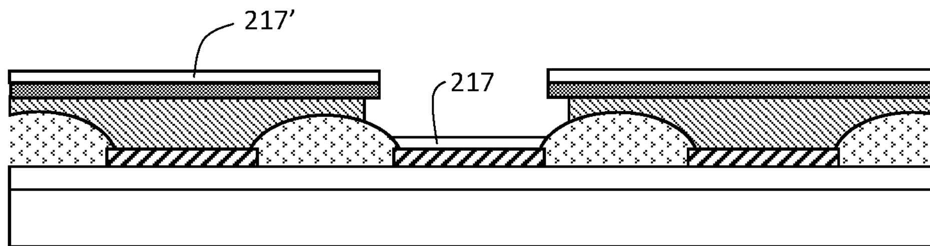



FIG. 8B

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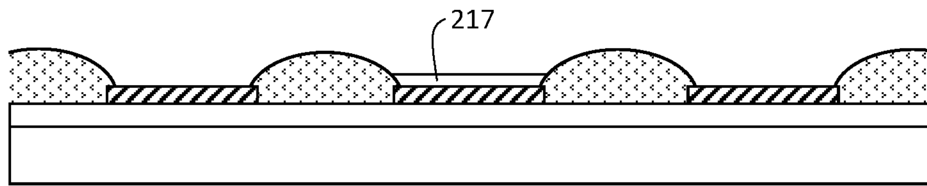


FIG. 8C

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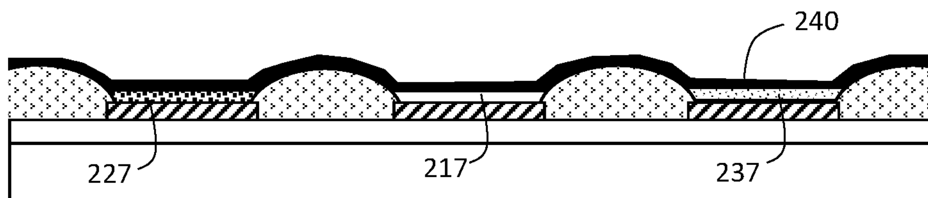


FIG. 8D

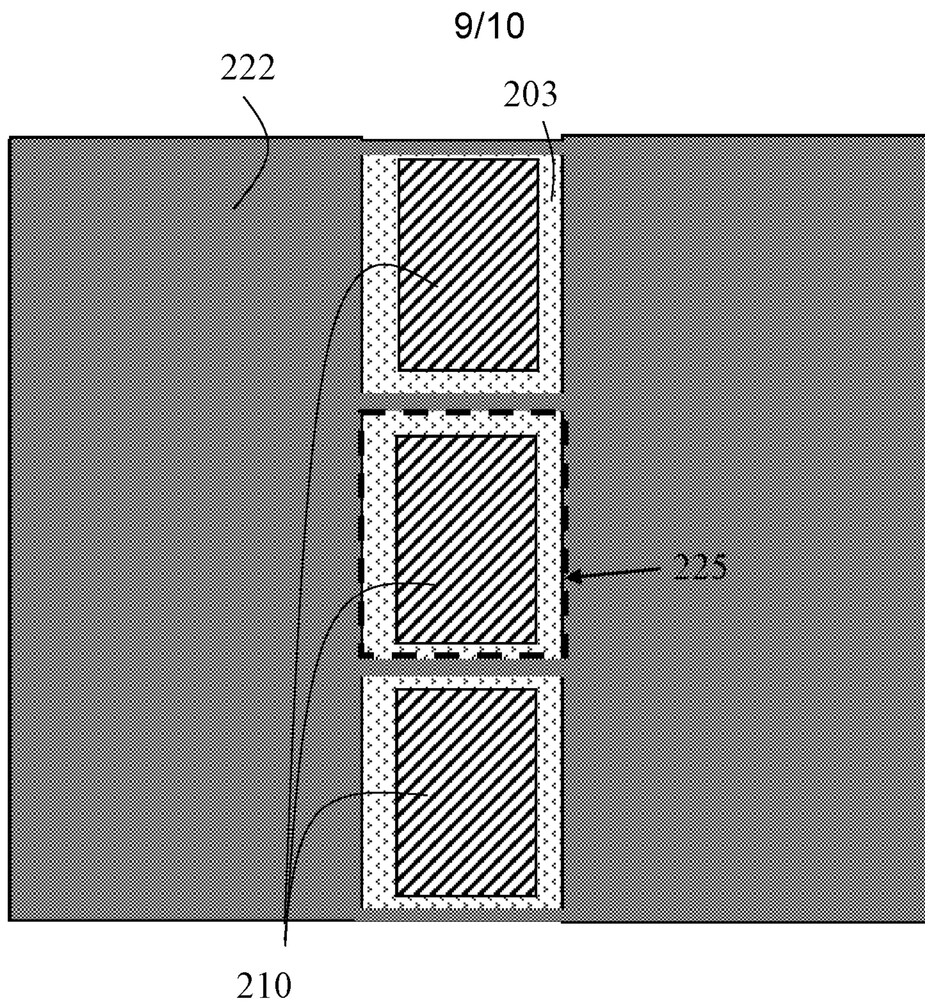


FIG. 9

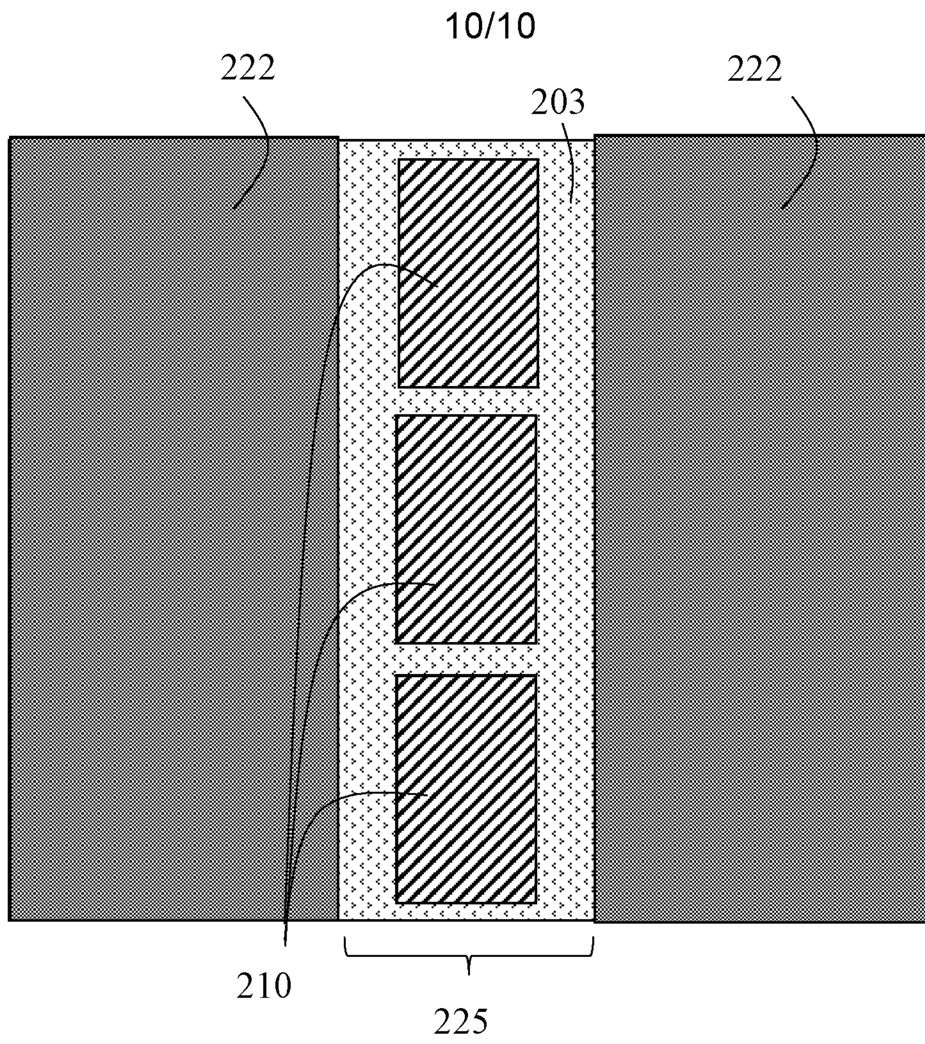


FIG. 10

**INTERNATIONAL SEARCH REPORT**

International application No.
**PCT/US2020/017293**

**A. CLASSIFICATION OF SUBJECT MATTER**

**G03F 7/32(2006.01)i, G03F 7/42(2006.01)i, G03F 7/029(2006.01)i, H01L 51/00(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
G03F 7/32; C11D 7/50; G03F 7/00; H01L 31/0216; H01L 31/0236; H01L 51/00; H01L 51/50; H01L 51/52; H01L 51/56; G03F 7/42; G03F 7/029

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: fluoropolymer, resist, undercut, hydrofluoroether

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| Y | US 2017-0219921 A1 (ORTHOGONAL, INC.) 03 August 2017 paragraphs [0020]-[0087], claims 1-30 and figures 1A-2E | 1-20 |
| A | US 2017-0256754 A1 (ORTHOGONAL, INC.) 07 September 2017 paragraphs [0030]-[0069] and figures 1-4 | 1-20 |
| A | US 2018-0102443 A1 (ALTA DEVICES, INC.) 12 April 2018 paragraphs [0018]-[0060] and figures 1-4D | 1-20 |
| A | US 2012-0305897 A1 (CHRISTOPHER OBER et al.) 06 December 2012 paragraphs [0116]-[0117], claim 1 and figure 21 | 1-20 |

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
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| 12 June 2020 (12.06.2020) | **12 June 2020 (12.06.2020)** |


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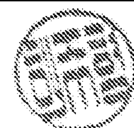
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